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INTERNAL STRUCTURE OF SILICATE MINERALS THAT GELATINIZE WITH ACID*

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ABSTRACT

A list of silicate minerals that are reported to gelatinize on being treated with acid was compiled and arranged according to a classification based on the internal structures of the minerals. From an examination of this data it is concluded that the following classes of minerals will gelatinize, if they are vulnerable to acid attack.

1. Those minerals containing silicate radicals of small molecular weight, namely orthosilicates, pyrosilicates, and possibly silicates containing ring structures of three silicon atoms.

2. Those minerals with large continuous silicon-oxygen networks that will disintegrate into units of low molecular weight.

   (a) Disilicates containing appreciable ferric iron in the silicon-oxygen sheets.

   (b) Minerals of the silica type with three-dimensional networks that contain aluminum in the ratio of at least two aluminum atoms to three silicon atoms.

Minerals that separate insoluble silica, instead of gelatinizing, upon being treated with acid, are characterized by silicon-oxygen structures of large dimensions that do not disintegrate into small units under acid attack. These are SiO_3 chains, Si_4O_{11} double chains,

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Si_2O_5 sheets not containing large amounts of ferric iron replacing silicon, and three-dimensional networks having an aluminum content less than the ratio of two aluminum atoms to three silicon atoms.

The exceptions to these rules are briefly discussed.

INTRODUCTION

Before the discovery of the methods of x-ray analysis, various attempts[1] were made to deduce the constitution of the silicate minerals by chemical means. Minerals were subjected to the action of acids, alkalies and other reagents, and from their different behaviors different types of structure were inferred, many of which have been found to be inadequate or erroneous through the more direct x-ray methods of analysis that were subsequently developed.

Now that there is a fairly detailed knowledge of the internal structure of the major groups of silicate minerals, it becomes of interest to reverse the process of study and to examine the chemical properties of these minerals in the light of their known constitution. Various physical qualities such as hardness, cleavage, twinning laws, and optical properties, have already been qualitatively or quantitatively explained in terms of the internal structures. The restricted chemical composition of some of the silicates and the greatly varied composition of others, which can undergo isomorphous replacements, are now seen to be a consequence of specific requirements of the various crystal structures. Among the few examples of a dynamic chemical property of the silicates that has been correlated with their structure are the base-exchange relations of the zeolites,[2] and the water-absorbing behavior of the clay minerals.[3]

In this paper, the property possessed by a number of silicate minerals of gelatinizing on being treated with acids will be considered in terms of their structure. This property seems especially suitable for examination because it has been noted among many different types of silicate minerals, and it so directly involves their fundamental silicon-oxygen frameworks.

The hypothesis is presented that in order for a mineral to gelatinize, its siliceous structure must be of such a nature that, when attacked by an acid, it will break down into units of small molecular weight not containing more than some small maximum number of silicon atoms.

The nature of the liberated silica is not viewed here with the care or the aim that Tschermak[4] had in mind, when he tried to identify various silicic acids which he believed were given off by the silicate minerals on acid treatment. Silicate minerals that are not attacked, or only slightly attacked by acids, are not considered in this paper except where decomposition may be expected from their group relations or from their composition. Neither are those silicates considered that contain additional acid radicals as major constituents (spurrite, thaumasite, etc.).

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[1] For a review of these attempts, see Doelter, C., *Handbuch der Mineralchemie*, **2** (1), 61–109 (1914). Clarke, F. W., *U. S. Geol. Survey, Bull.* **588** (1914).

[2] Taylor, W. H., *Proc. Roy. Soc.* (London), **A 145,** 80 (1934).

[3] Hendricks, S. B., and Jefferson, M. E., *Am. Mineral.*, **23,** 863 (1938).

[4] Tschermak, G., *Sitz. Akad. Wiss. Wien., Math.-Naturw. Klasse, Abt.* **1,** 217 (1906).

METHOD OF TESTING MINERAL POWDERS

The silicate minerals that are decomposed by acid treatment may be placed in one of two classes, following Brush and Penfield[5] (pp. 108 and 109) but reversing their order, namely:

(1) Those that separate insoluble silica without forming a jelly.
(2) Those that form a jelly (gelatinization).

That it is possible to discriminate between these two classes with practical precision is shown by the fact that this discrimination is required in the well known determinative scheme of Brush and Penfield. Their method of treating the minerals with hydrochloric or nitric acids might be adopted as a reference standard for the purposes of this discussion, although it is usually not necessary to continue the boiling until only 1 ml. of solution remains. Their method of treatment is as follows:

> (p. 278) " . . . treat one or two ivory-spoonfuls[6] of the *finely powdered* material in a test tube with from 3–5 c.c. of hydrochloric acid, and boil until not over 1 c.c. remains."

(1) For those minerals that separate insoluble silica without forming a jelly (without gelatinization), they state: (p. 281)

> "When the powder is first shaken up with the cold acid the liquid will generally appear milky, owing to the fine, suspended material; when boiled, however, the liquid becomes translucent, although the separated silica prevents it from becoming perfectly clear. After a little experience one can usually decide from appearances whether the insoluble material is *separated silica* or the *undecomposed mineral;* . . . "

The mineral is decomposed but is not completely soluble to a clear filterable solution; the presence of separated silica is characteristic. This separated silica is variously described in the literature as being slimy, gelatinous, pulverulent, flocculent, or sandy; or to form a skeleton of silica, a deposit of silica, or to separate the silica in scales. A comparison of the character of the separated silica from several minerals of class 1 does not indicate any necessity for such distinctions. In fact, some of the terms are misleading. Thus both apophyllite and chabazite are stated by Dana to yield "slimy silica" and xonotlite to yield "pulverulent silica," but comparative tests made on these minerals indicated no such essential difference between the separated silicas.

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[5] Brush, G. J., and Penfield, S. L., *Determinative Mineralogy and Blowpipe Analysis.* 16th ed., Wiley, New York (**1898**).

[6] In order to place the reaction on a somewhat more quantitative basis, some tests were made as to the quantity of ground mineral sample in an "ivory spoonful." Using an ivory spoon (kindly loaned by Prof. Switzer of Yale) of the type and size illustrated in Fig. 42, p. 41, of Brush and Penfield, it was found that such a spoonful, the bowl of the spoon measuring about 13 by 5 mm. and about 1 mm. deep, contained from 0.04 to 0.05 ml. of 100-mesh mineral powder when neither heaped nor levelled off. For a mineral of sp. gr. 2 to 3, the sample weighed about 0.10 to 0.15 gram; for sp. gr. of 3 to 4, the sample weighed about 0.15 to 0.20 gram.

The character of the "separated silica" varies slightly for different minerals. It usually appears isotropic under the microscope (chabazite, wollastonite, pectolite, sturtite) with a refractive index of about 1.45. For apophyllite, the separated silica appeared birefringent. For some minerals the separated silica sharply retains the size and shape of the original mineral grains whereas for other minerals the grains tend to spread and fray out.

(2) For those minerals that form a jelly, Brush and Penfield state: (p. 278)

> "The mineral should go wholly into solution, unless difficultly soluble, and when the volume becomes small the contents of the tube should *thicken*, owing to the separation of *gelatinous silicic acid*."

It is obvious that the expression "separation of gelatinous silicic acid" means the *formation of a jelly*.

The procedure to be followed is explained in greater detail by Brush and Penfield on page 109. In making such tests it is well to follow the caution to mix the ground sample first with 1 ml. of water before adding the acid, in order to prevent caking. For 2 or 3 ml. of acid, 1 ivory spoonful is ample. For some minerals tested—nepheline, hemimorphite, olivine, tephroite, leucophoenicite—it was not necessary to "boil until not over 1 c.c. remains." On gentle heating, the minerals readily dissolved and formed a stiff jelly with very little diminution of total volume of liquid.

The specifications of class (2) "Those that form a jelly," under standard conditions—1 ivory spoonful of at least 100 mesh powder with 3 ml. acid—may then be defined as follows: Completely soluble to a clear filterable solution which when gently heated and allowed to stand for a short time (nepheline, for example) or if necessary, boiled with consequent reduction of volume of liquid (olivines), becomes thick from the development of gelatinous silica, so rigid that nothing runs out when the test tube is inverted.

Minerals that gelatinize easily, such as nepheline, hemimorphite, tephroite, readily set to a non-filterable rigid gel on gentle warming if 2 ml. concentrated hydrochloric acid is added to the mineral powder already shaken with 1 ml. of water. Perhaps it would set similarly in the cold if allowed to stand sufficient time. The mineral and liquid should be continuously agitated for a while to prevent "setting" of mineral grains at the bottom of the tube. This is easily done by holding the tube at its upper end between the thumb and index finger of one hand and gently tapping the bottom of the tube with a finger of the other hand.

Other minerals, such as olivine, are less easily decomposed and may require boiling and consequent reduction of volume of liquid. Undecomposed mineral may remain in the bottom of the tube even if the solution sets to a rigid gel.

Minerals of class 2 may be described as decomposed by acid with gelatinization, if the term gelatinization be restricted to mean that a rigid jelly is formed.

The expressions "separation of gelatinous silicic acid," "formation of gelatinous silica," "gelatinizes," "affords a jelly," found in the literature usually imply the formation of a rigid jelly. The phrase "separation of gelatinous silica" however is ambiguous as it may be interpreted as yielding masses of gelatinous silica without the solution setting to one rigid mass of jelly. Thus the action of acid on the two minerals, leucophoenicite and alleghanyite, of very similar composition, may be described for both minerals as yielding a "separation of gelatinous silica," but whereas leucophoenicite readily sets to a rigid jelly, repeated tests on various samples of alleghanyite failed to yield a rigid jelly although masses of gelatinous silica readily separate. In the terminology here used leucophoenicite is decomposed by acid with gelatinization whereas alleghanyite is decomposed by acid without gelatinization, although masses of gelatinous silica separate out.

Thus, although the decomposable minerals may be grouped into two classes for practical reasons, the division may not be altogether sharp and definite and transitions may exist. The filtered solution of a mineral of class 1, which does not gelatinize, that is, does not set to a rigid jelly, under the conditions described, might possibly, on sufficient reduction of volume, result in a jelly-like mass due to the small quantity of silica that went into solution though the bulk of the silica separated out as insoluble.

Compilation of Data

A list of minerals that gelatinize has been compiled mainly from the tables in the book by Brush and Penfield and from the extensive tables in the Geological Survey Bulletin by Larsen and Berman.[7] In the latter, a distinction is made between silicates that "gelatinize" and those that are "soluble in HCl." The writer has assumed that these two expressions are equivalent. Whether on addition of an acid there is immediate gelatinization or whether the solution must be evaporated for the jelly to appear is largely a matter of concentration of acid and the volume of acid applied to a given weight of the mineral. Therefore, minerals indicated as showing either behavior have been included in the compilation. Because the expression "soluble in HCl" is used loosely by some authors to mean simply that the mineral is decomposed by acid, without implying anything as to the nature of the silica which is separated, special care was taken with minerals that were so described to compare the data from several sources.

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[7] Larsen, E. S., and Berman, H., *U. S. Geol. Survey, Bull.* **848** (1934).

The compiled list of minerals was first classified according to the scheme outlined by Berman.[8] Then the major divisions were rearranged in accordance with Bragg's classification,[9] in which the orthosilicates are considered first, as this arrangement is more convenient for this discussion. Berman is careful to point out that although the major structural types of silicate minerals have been recognized through x-ray studies, the actual number of species that have been completely analyzed is small, something like 10–15 per cent of the total number. He frankly admits "the probability that a considerable number of minerals will be found, when more structural data are available, to have been misplaced in the classification." Some of the anomalies to be noted later may arise from such misplacements. In spite of the uncertainties, however, Berman's classification is a valuable extension and application of the new structural principles, and it greatly facilitated the present study.

The various type structures that form the basis of modern classifications of the silicate minerals are illustrated in the following cut from Berman's paper, and his numbering of the figures is followed in this paper.

The following table should be carefully compared with the one given by Berman. All minerals that are absent from the table are not reported to gelatinize. They are undecomposed by acid or only slightly decomposed, are decomposed with separation of silica, or, for a few minerals, have no data as to their behavior towards acid given for them. Some discrepancies encountered in comparing the various sources of information are noted in the footnotes to the table, and a few other discrepancies are discussed at different places in the text.

In noting the minerals that do not appear in the table because of their non-decomposition, or only slight decomposition by acid, a rough correlation between non-decomposition and internal structure soon becomes apparent. Brush and Penfield[10] have remarked that "orthosilicates are more soluble in acids than metasilicates and polysilicates." However,

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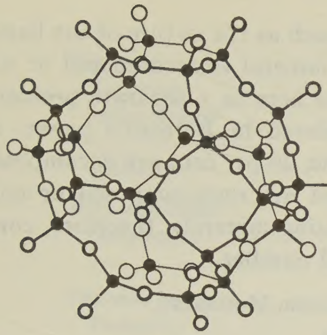
[8] Berman, H., *Am. Mineral.*, **22**, 342 (1937).

[9] Bragg, W. L., *Atomic Structure of Minerals*. Cornell Univ. Press (**1937**).

[10] *Loc. cit.*, p. 108.



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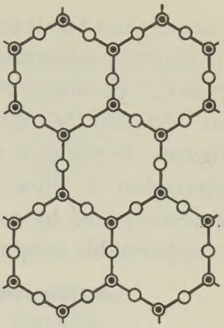

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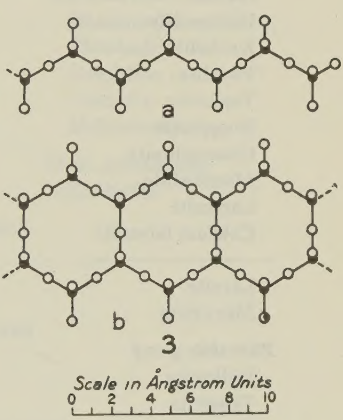

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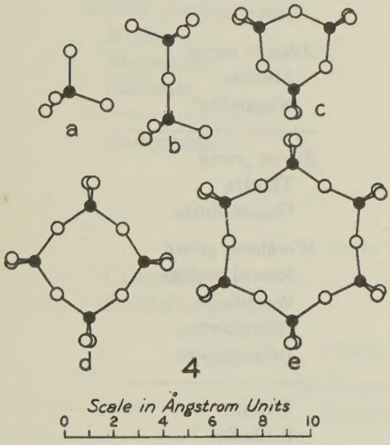

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Linkages of silicon-oxygen tetrahedra. Black, silicon, with or without aluminum; white, oxygen. After Bragg.

Fig. 1. One example of the Silica type, SiO_2; three-dimensional linkage.

Fig. 2. One example of the Disilicate type, Si_2O_5; two-dimensional linkage.

Fig. 3. Metasilicate type; (a) SiO_3, single-chain linkage; (b) Si_4O_{11}, double-chain linkage.

Fig. 4. (a) Orthosilicate type, SiO_4; independent tetrahedra. (b) Pyrosilicate type, Si_2O_7; paired tetrahedra. (c) Ring-linkage, Si_3O_9. (d) Ring-linkage, Si_4O_{12}. (e) Ring-linkage, Si_6O_{18}.

The gelatinizing minerals have silicon- (and aluminum-) oxygen linkages shown in the following figures.

Figure 1, with the amount of aluminum that replaces silicon equal to, or exceeding the ratio of, two aluminum atoms to three silicon atoms.

Figure 2, with a large amount of ferric iron replacing silicon.

Figures 4*a*, 4*b*, and possibly 4*c*.

Minerals that separate insoluble silica, instead of gelatinizing, have linkages shown in Figs. 1, 2, 3*a*, and 3*b*, except for the compositions noted above for Figs. 1 and 2.

The data on the behavior of the ring linkages, 4*c*, 4*d*, and 4*e*, are meager.

factors other than the internal structure, such as the nature of the bases, are important in determining whether a mineral is decomposed or undecomposed,[11] so this matter is considered here as a separate problem.

About 350 silicate minerals are considered in Berman's paper. In rough figures, 35 per cent of these gelatinize, 20 per cent are decomposed with separation of silica, and 45 per cent are undecomposed or only slightly decomposed by acid. The gelatinizing minerals, therefore, comprise an appreciable proportion of the total number.

A Classified List of Gelatinizing Minerals

Orthosilicates

- *Olivine group*
  - Forsterite
  - Olivine
  - Hortonolite
  - Knebelite
  - Fayalite
  - Tephroite
  - Roepperite
  - Glaucochroite
  - Monticellite
  - Larsenite
  - Calcium larsenite

- Larnite
- Merwinite
- *Phenakite group*
  - Willemite
  - Troostite
  - Trimerite[1]
  - Dioptase
- *Humite Group*
  - Chondrodite
  - Humite
  - Clinohumite
- *Hodgkinsonite group*
  - Hodgkinsonite
  - Leucophoenicite

- Gageite[2]
- *Garnet group*
  - Andradite
  - Titanium garnet
  - Hibschite

- Sarcolite
- *Allanite series*
  - Allanite
  - Nagatelite[3]

- *Zircon group*
  - Thorite
  - Uranothorite
- *Woehlerite group*
  - Rosenbuschite
  - Woehlerite
  - Hiortdahlite
  - Johnstrupite

- Rinkite
- Rinkolite
- Mosandrite[4]
- Låvenite
- Britholite
- Hellandite
- Lessingite
- Abkumalite
- *Datolite family*
  - Datolite
  - Homilite
  - Gadolinite
- *Misc. orthosilicates*
  - Ilvaite
  - Eulytite
  - Agricolite

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[11] For example, beryllium, when it is the dominant base in a mineral, greatly influences the behavior of the mineral toward acid. In the orthosilicate phenakite group and the pyrosilicate hemimorphite family, only phenakite, Be_2SiO_4, and bertrandite, $Be_4Si_2O_7(OH)_2$, are undecomposed, and thereby stand conspicuously apart from the other members which are all attacked by acid.

Subsilicates

- *Kentrolite group*
  - Kentrolite
  - Melanotekite[5]

- Beckelite

- *Misc. subsilicates*
  - Cappelenite

- *Uranium silicates*
  - Uranophane
  - Sklodowskite
  - Kasolite
  - Soddyite

Pyrosilicates

- *Thalenite group*
  - Thalenite
  - Cerite
  - Rowlandite

- *Melilite group*
  - Melilite
  - Akermanite
  - Gehlenite

- Hardystonite

- *Barysilite group*
  - Barysilite
  - Ganomalite
  - Nasonite

- *Hemimorphite family*
  - Hemimorphite
  - Clinohedrite
  - Cuspidine
  - Custerite
  - Molybdophyllite

- *Misc. pyrosilicates*
  - Rankinite

Ring Structures

- Catapleiite[6]
- Eudialyte (eucolite)

Chain Structures

- *Wollastonite group*
  - Alamosite

- *Calcium metasilicate family*
  - Hillebrandite
  - Jurupaite
  - Afwillite

- *Misc. metasilicates*
  - Cenosite
  - Ussingite

Disilicates

- *Clay group*
  - Volchonskoite
  - Nontronite

- *Talc group*
  - Nepouite

- *Friedelite group*
  - Zeophyllite[7]
  - Gyrolite[8]

- *Misc. non-aluminum disilicates*
  - Okenite

- *Leptochlorite group*
  - Thuringite
  - Cronstedtite
  - Aphrosiderite

- *Vermiculite group*
  - Griffithite

- *Mica group*
  - Lepidomelane[9]

- *Misc. disilicates*
  - Ganophyllite

SILICA TYPE

Feldspar group
Celsian
Anorthite

Nepheline group
Nepheline
Kaliophilite
Kalsilite
Eucryptite

Cancrinite group
Cancrinite
Microsommite
Davyne

Sodalite group
Sodalite
Hackmanite
Noselite
Hauyne
Lazurite
Helvite
Danalite

Zeolite family
Stilbite group
Phillipsite[10]

Gismondite

Levynite

Thomsonite group
Thomsonite
Faroelite
Gonnardite
Ashcroftine

Natrolite group
Natrolite
Mesolite
Scolectite
Edingtonite

Misc. zeolites
Laumontite

Silicate minerals unclassified by Berman.

Allophane
Greenalite
Lovchorrite
Pilbarite
Tritomite
Yttrialite
Tscheffkinite
Zebedassite
Cebollite
Roeblingite
Orientite
Fraipontite
Bulfonteinite
Yeatmanite
Silicomagnesiofluorite

The discrepancies noted below and in different places in the text may be more apparent than real, because of the possible loose usage of the expressions "decomposed by HCl" and "soluble in HCl." The writer has interpreted the former expression to mean "decomposed by HCl with separation of silica," and the latter to be synonymous with "gelatinizes with HCl," but this may not have been the meaning intended by the various authors.

[1] Trimerite is reported as soluble in HCl by Larsen-Berman; as decomposed by HCl without gelatinization by Brush-Penfield.

[2] Gageite is reported as decomposed by HCl by Larsen-Berman; as dissolved at once in warm dilute nitric acid by Palache, *U. S. Geol. Survey, Prof. Paper* **180,** 111 (1930).

[3] Nagatelite is reported as soluble in HCl by Larsen-Berman. In the original description it is said to be easily decomposed by HCl leaving a white flocculent residue—Iimori et al., *Sci. Pap. Inst. Phys. Chem. Res. Tokyo,* **15,** 83 (1931).

[4] Mosandrite is reported as soluble in HCl by Larsen-Berman; as decomposed without gelatinization by Brush-Penfield.

[5] Melanotekite is reported as decomposed by HNO_3 by Larsen-Berman; as not giving a good jelly by Brush-Penfield.

[6] Catapleiite is reported as gelatinizing by Larsen-Berman; as decomposed by HCl without gelatinization by Brush-Penfield.

[7] Zeophyllite is reported as gelatinizing by Larsen-Berman; as soluble in HCl with the separation of flocculent, slimy silica by Hintze, *Handbuch der Mineralogie*, Ergänzungsband, Lief. **4,** 747 (1937).

[8] Gyrolite is reported to gelatinize with HCl by Brush-Penfield; easily soluble in dilute acids by Doelter, *Handbuch d. Mineralchemie*, **2** (1) 470 (1914); decomposed by HCl by Larsen-Berman.

Berman suggests that gyrolite and centrallassite may be identical, but all authorities agree that centrallassite is decomposed by HCl without gelatinization.

[9] Lepidomelane is said to gelatinize by both Brush-Penfield and Larsen-Berman; as easily decomposed by HCl, depositing silica in scales by Dana, *System of Mineralogy*, 6th ed.

[10] Phillipsite is reported as gelatinizing by Larsen-Berman; as decomposed by HCl without gelatinization by Brush-Penfield.

DISCUSSION

Orthosilicates. Figure 4a.

As a working hypothesis for the following discussion, it is assumed that in order for a mineral to gelatinize its siliceous structure must be of such a nature that, when attacked by an acid, it will break down into units of small molecular weight not containing more than some small maximum number of silicon atoms. Under this hypothesis, it follows that minerals containing discrete SiO_4 groups, which might be pictured as being dislodged from the mineral and going into solution as simple orthosilicic acid, H_4SiO_4, would most readily gelatinize. This would account for the ready gelatinization that characterizes minerals of the olivine, phenakite, humite, hodgkinsonite, woehlerite and datolite groups. All together, forty-nine species of the orthosilicate type are reported to gelatinize.

There are conflicting data for the behavior of trimerite, gageite, nagatelite, mosandrite and melanotekite, as noted in the footnotes to the table. Norbergite of the humite group is definitely stated, in the original description[12] to be soluble in warm HCl with the separation of silica. This behavior is anomalous for an orthosilicate.

As mentioned in the section on method of testing mineral powders, alleghanyite separates a mass of gelatinous silica but does not form a rigid jelly.

Garnets are also a potential source of gelatinous silica, because of their content of discrete SiO_4 groups. However, nearly all garnets are only slightly affected by acid, and the only varieties that are notably attacked to give gelatinous silica are andradite and the titanium garnets. Andradite is the first of several examples that show the weakening influence of ferric iron when it replaces aluminum in a silicate structure. The high content of ferric iron (17–23% Fe_2O_3) in the titanium garnets is probably also reponsible for their gelatinization. The garnetoid mineral, hibschite,[13] is soluble in HCl, which shows that the substitution of water for silica likewise weakens the garnet structure toward acid attack.

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[12] Bygden, A., in Geijer, P., *Geol. För. Stockholm, Förh.*, **48,** 84 (1926).

Subsilicates

The nature of the silicate groups in the subsilicates, kentrolite, melanotekite, beckelite, cappelenite, and in the uranium silicates, is unknown. Probably independent SiO_4 groups are present. The gelatinization of these minerals, under the working hypothesis, points to discrete units involving only a few silicon atoms or to larger networks that would disintegrate into smaller units under acid attack. Melanocerite is the only mineral among the subsilicates that separates insoluble silica.

Pyrosilicates. Figure 4*b*.

That the pyrosilicate group or radical containing two silicon atoms will undergo gelatinization is abundantly illustrated by the soluble members of the thalenite, melilite, barysilite and hemimorphite groups. All together, there are sixteen gelatinizing minerals of the pyrosilicate type. Murmanite of the hemimorphite family and astrophyllite, both reported to be decomposed with a separation of silica, stand as exceptions.

With this pyrosilicate unit, and all of the other condensed silicate structures which arise from mutual sharing of oxygen among adjacent silicon atoms, the reasonable assumption is made that the silicon-oxygen binding, -Si-O-Si-, among these adjacent silicons is strong enough to resist any attack by acids. The integrity of these condensed structures is also illustrated in the prevailing belief that no major physical weakness of a crystal, such as a prominent cleavage, readily transects such structures.

Ring structures. Figure 4*c*.

If Berman's postulate that eudialyte and catapleiite have closed silicon-oxygen rings containing three silicon atoms is correct, these minerals would offer examples of a condensed silicate unit of such dimensions gelatinizing. The evidence from catapleiite is marred by a discrepancy noted in the footnote to the table. On the other hand, steenstrupine, whose constitution is also interpreted by Berman as involving

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[13] Belyankin, D. S., and Petrov, V. P., *Am. Mineral.*, **26**, 450 (1941).

Si_3O_9 rings, is reported to be "entirely decomposed by acids," and apparently not gelatinizing.

Chain structures. Figures 3a, 3b.

Silicon-oxygen structures of considerable dimensions are first encountered in the classification at this point. There is a sudden drop in the number of minerals that are attacked by acids. As illustrated in Figs. *3a* and *3b*, the chain structures are narrow in width, but extend continuously along their length. Minerals made up of such large structures would not be expected to gelatinize.

The amphiboles, pyroxenes (with the exception of johannsenite), the members of the rhodonite series of the pyroxenoid family, and the miscellaneous pyroxenoids are undecomposed, and therefore can offer no evidence as to the behavior of the chain structures under effective acid attack. Johannsenite[14] is completely decomposed by acid with separation of silica.

Among the hornblendes aluminum substitutes for silicon in the chain up to a maximum amount of one aluminum to three silicons,[15] i.e., up to a composition, $AlSi_3O_{11}$, for the amphibole chain. Apparently a substitution of this nature and magnitude does not lower the resistance of these minerals towards acids. A high content of ferric iron (15–30% Fe_2O_3), associated with but not incorporated in the silicon-oxygen chains, is without marked effect as shown by the non-decomposition of aegirite, acmite, riebeckite, and crocidolite.

Members of the wollastonite group and some members of the calcium metasilicate family separate silica, and this would be in accord with the concept of the integrity of the silicon-oxygen chains.

Wollastonite is reported in most references as separating insoluble silica, but is said in Rutley's *Mineralogy*[16] to gelatinize. This supposedly single species has been resolved into a triclinic modification (wollastonite) and a monoclinic modification (parawollastonite).[17] The behavior of these two modifications towards acid seems deserving of further study because of Barnick's conclusion[18] that their internal structure is made up of Si_3O_9 rings rather than SiO_3 chains.

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[14] Schaller, W. T., *Am. Mineral.*, **23,** 575–582 (1938).

Results obtained by W. T. Schaller (personal communication) indicate that for members of the isomorphous series between johannsenite, diopside, and hedenbergite, the degree of attack by acid is proportional to the quantity of manganese present.

[15] Warren, B. E., *Zeits. Krist.*, **72,** 493 (1930).

[16] Rutley's *Elements of Mineralogy* by H. H. Read. 23rd ed., London (**1936**).

W. T. Schaller has found that wollastonite from Potash Sulphur Springs, near Hot Springs, Arkansas, gelatinizes readily.

[17] Peacock, M. A., *Am. Jour. Sci.*, **30,** 495–529 (1935).

[18] Barnick M., *Naturwissenschaften*, **23,** 770–771 (1935).

There are conflicting data on the behavior of searlesite.[19] J. J. Fahey of the Geological Survey Chemical Laboratory, who recently analyzed a specimen of searlesite from Sweetwater County, Wyoming, reports that[20] "searlesite decomposes when boiled for 15 minutes with 1:1 HCl, leaving a siliceous skeleton which retains the form of the original crystal fragment. Treatment with cold 1:1 HCl for 24 hours causes only a partial decomposition of the mineral." This is the behavior one would expect of a mineral having an extensive silicon-oxygen condensed structure.

The concept of the integrity of the silicon-oxygen chains throws into prominence those minerals of this part of the classification that are said to gelatinize: alamosite, hillebrandite, jurupaite, afwillite, cenosite, and ussingite. Alamosite with its simple composition, $PbSiO_3$, is outstanding among these exceptions. The question may be raised whether the formula of hillebrandite should not be written as $Ca_2SiO_4 \cdot H_2O$ and the mineral classified among the orthosilicates.

Disilicate type. Figure 2.

The condensed silicon-oxygen structure, which forms the basis for this part of the classification, extends continuously in two directions, forming a sheet-like framework. This framework bestows on platy minerals, such as the micas and the clays, their peculiar physical and chemical properties. Treating biotite and phlogopite with acids to obtain plates of hydrated silica is a well known laboratory experiment among students of mineralogy. As with the chain structures, a large number of minerals of the disilicate type are insoluble in acid.

Aluminum can freely substitute for silicon in the sheet structure, giving a continuous series of composition for the structure of Si_4O_{10}, $AlSi_3O_{10}$, $Al_2Si_2O_{10}$, and Al_3SiO_{10}, the last composition being approached in seybertite and xanthophyllite of the clintonite group. This considerable entrance of aluminum into the two dimensional silicon-oxygen sheet apparently does not cause any corresponding change in the behavior of disilicate minerals toward acids. This appears remarkable in light of the marked weakening effect that aluminum shows in the three dimensional silicon-oxygen networks to be discussed later.

A glance at the list of minerals of the disilicate type which are reported to gelatinize reveals that a high content of ferric iron is a feature common to some of them. The weakening effect of ferric iron on silicate structures, already noted with andradite and the titanium garnets, is indicated. However, an additional necessary condition would seem to be that the ferric iron must be in the silicon-oxygen sheet itself to promote the disruption of this sheet into smaller units. Ferric iron within the sheet structure has been recognized in cronstedtite,[21] and possibly this condition may be found in the other gelatinizing minerals, rich in ferric iron, namely, volchonskoite, some nontronites (for example, the type nontronite), thuringite, and lepidomelane.

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[19] Larsen, E. S., and Hicks, W. B., *Am. Jour. Sci.*, **38**, 437 (1914). Foshag, W. F., *Am. Mineral.*, **19**, 268 (1934).

[20] Personal communication.

The entrance of an ion-like ferric iron, which is appreciably larger than silicon, into the tetrahedral position of a silicate structure calls for a brief examination of the geometrical restrictions that must be complied with. This ion must have a coordination number of four, i.e., it must be of such a size, neither too small nor too large, so that it can hold four oxygen ions around itself in a stable tetrahedral arrangement. The coordination number of a cation with respect to any anion is determined by the geometrical quantity ρ, known as the radius ratio and defined as $\rho = R^+/R^-$, where R^+ and R^- are the radii of the cation and anion respectively.

The radius ratio for ferric iron with respect to oxygen, when calculated according to the method given by Pauling[22] starting with his value of 0.60Å for the empirical radius of ferric iron, is 0.45. This places ferric iron between quadrivalent germanium and divalent magnesium with respect to its coordinating number (see Pauling's table 48–52), and therefore, just within the range, delimited by the values of the radius ratio, in which tetrahedral coordination is possible.

The calculation shows that ferric iron is a borderline ion among those that can assume a tetrahedral coordination, and suggests that minerals containing this ion in such a coordination would be rare. At present ferric iron in a tetrahedral coordination is known among natural minerals only in cronstedtite and in small amounts in iron-bearing orthoclase.[23]

Glauconite is an example of a mineral of the disilicate class, rich in ferric iron, with the ferric iron in octahedral positions outside the silicon-oxygen sheets.[24] Those samples of glauconite that are decomposed by acid separate silica.[25] Experiments by Hutton and Seelye[26] show that 80–90 per cent of the silica is insoluble and remains on the filter.

The gel-forming nature of zeophyllite, gyrolite, okenite, aphrosiderite, griffithite, ganophyllite, and nepouite, cannot be explained on the basis that these minerals are made up of continuous sheet structures. It seems unlikely that nepouite, a mineral with the structure of antigorite,[27] should dissolve completely in HCl as Glasser[28] reports.

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[21] Hendricks, S. B., *Am. Mineral.*, **24**, 529 (1939).

[22] Pauling, L., *Nature of the Chemical Bond*. 2nd ed. pp. 345–350 and 380–382. Cornell Press (**1940**).

[23] Faust, G. T., *Am. Mineral.*, **21**, 735 (1936).

[24] Hendricks, S. B., and Ross, C. S., *Am. Mineral.*, **26**, 683 (1941).

[25] Smulikowski, K., *Arch. Min. Tow. Nauk. Warzaw*, **12**, 145–180 (1936). Turrentine, J. W., et al., *Ind. Eng. Chem.*, **17**, 1177–1181 (1925).

[26] Hutton, C. O., and Seelye, F. T., *Am. Mineral.*, **26**, 595–604 (1941).

Apophyllite, listed among the miscellaneous non-aluminum disilicates by Berman, is made up of what Bragg calls the tetragonal type of silicon-oxygen sheet, in contrast to the hexagonal type of silicon-oxygen sheet shown in Fig. 2. The silicon-oxygen tetrahedra form rings of four and eight linked groups instead of rings of six linked groups.[29] The mineral is decomposed by hydrochloric with separation of silica. Skeletonized apophyllite, with composition similar to that of opal, has recently been described by Bailey.[30]

Silica type. Figure 1.

The fundamental silicon-oxygen framework possessed by minerals of this category is a three dimensional structure which results from the fullest sharing of oxygen among adjacent silicon atoms. This three-dimensional framework seems more fragile when compared with the sheet structure of the previous section, in that an appreciable substitution of the silicon atoms by aluminum renders it vulnerable toward profound attack by acid with consequent gelatinization. The presence of aluminum in a ratio of two or more aluminum to three silicon results in a structure that can gelatinize. The frameworks of many of the minerals of this class have large channels that allow base-exchange reactions and movements of water. These open channels make such minerals peculiarly susceptible to acid attack.

Among the feldspars, only celsian and anorthite are commonly reported to gelatinize, and these have an aluminum to silicon ratio of 1:1. The plagioclase feldspars are progressively more decomposed by acid as the composition changes from albite, which is unattacked, to anorthite, which gelatinizes. Bytownite, as well as anorthite, is said by Iddings[31] to gelatinize. The aluminum to silicon ratio of the least calcic bytownite is around 3:4. However, the exact relation between composition and gelatinization is obscured here because the representatives of such a large part of the plagioclase series are resistant to acid.

The fourteen minerals of the nepheline, cancrinite, and sodalite groups have an aluminum to silicon ratio of 1:1, and they all gelatinize.

The aluminum to silicon ratio in the scapolite series varies from 1:3 to 1:1, and these minerals, like the plagioclase feldspars, are progressively more decomposed by acid as the aluminum to silicon ratio becomes larger. However, the data on the behavior of these minerals toward acid is not very satisfactory. There are conflicting reports on whether meionite, the high-aluminum end member, gelatinizes or separates silica.[32]

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[27] Caillere, S., *Bull. soc. franc. mineral.*, **59**, 293–294 (1936).

[28] Glasser, E., *Ibid.*, **30**, 17(1907).

[29] Taylor, W. H., and Náray-Szabó, St., *Zeits. Krist.*, **77**, 146–158 (1931).

[30] Bailey, E. H., *Am. Mineral.*, **26**, 565–567 (1941).

[31] Iddings, J. P., *Rock Minerals*, 2nd ed., p. 206. New York (**1911**).

The zeolites are an excellent group of minerals for studying the relation between composition and gelatinization in three-dimensional structures, because such a large number of them succumb to attack by acid, with or without gelatinization. Rinne[33] has made detailed microscopic observations on the behavior of cleavage pieces or oriented sections of some of the zeolites subjected to the action of acids.

Among the zeolites, a general rule is apparent that those species having an aluminum to silicon ratio of 2:3, or higher, will yield gelatinous silica. The sole exception, which gelatinizes with a lower aluminum to silicon ratio, is laumontite (13:27).

Epidesmine (11:29) is said by Larsen and Berman to gelatinize, but this is believed to be in error. In Hintze's *Handbuch*,[34] this species is said to dissolve in hydrochloric acid with the separation of sandy, slimy silica. Furthermore, Pabst[35] has recently shown the identity of epidesmine, stellerite, and stilbite, and all authorities agree that the last two minerals decompose without gelatinization. Erionite is erroneously reported[36] to be easily soluble, although in the original description[37] it is said to be "soluble in HCl with extreme difficulty. Silica separates as fine sand with no gelatinization."

Two exceptions to the general rule in the other direction, namely, minerals with a ratio of 2:3 or higher that succumb to acid attack but do not gelatinize, are wellsite (18:22) and arduinite (2:3). There are eleven zeolites that gelatinize and eleven zeolites that separate silica which securely establish the boundary ratio of two aluminum to three silicon.

Minerals unclassified by Berman

Among the gelatinizing minerals unclassified by Berman, allophane is of special interest, because it is one of a very few minerals that have been demonstrated by *x*-ray and dehydration studies[38] to be truly amorphous. An unorganized amorphous state would seem especially favorable for gelatinization. Such materials as the siliceous glasses[39] are amorphous but contain extensive, though irregular silicon-oxygen networks, and substances of this nature which might be vulnerable to acid attack would not be expected to gelatinize.

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[32] Dana's *System of Mineralogy*, 6th ed., p. 468 (1920).

[33] Rinne, F., *Centralbl. Mineral. Geol. Palaeont.*, 594–601 (1902).

[34] Hintze, C., *Handbuch d. Mineralogie*, Ergänzungsband, Lief. **1**, 157 (1936).

[35] Pabst, A., *Mineral. Mag.*, **25**, 271 (1939).

[36] 1st appendix to 6th ed. Dana's *System of Mineralogy*.

[37] Eakle, A. S., *Am. Jour. Sci.*, **6**, 67 (1898).

[38] Ross, C. S., and Kerr, P. F., *U. S. Geol. Survey, Prof. Paper* **185-G**, 144–148 (1934).

[39] Zachariasen, W. H., *Jour. Am. Chem. Soc.*, **54**, 3841 (1932).
Warren, B. E., and Loring, A. D., *Jour. Am. Ceram. Soc.*, **18**, 269 (1935).

The report that greenalite is soluble in acids is not in harmony with the fact that it gives *x*-ray powder pattern of serpentine.[40] Very likely, the word "soluble" is used loosely to mean that the mineral is decomposed by acid. When the time comes for the minerals of this section to be classified, it is apparent that their gel-forming nature must be considered.

GELATINIZATION AFTER IGNITION

A number of minerals that do not gelatinize in their natural state will do so after being ignited. Examples of these are serpentine, zoisite, epidote, and the garnets. During ignition a new phase is formed which possesses the quality of gelatinizing. With serpentine it has been long known[41] that the new phase is olivine and this identification was recently checked[42] through *x*-ray powder photographs of the calcined product.

ACKNOWLEDGMENTS

The writer expresses his thanks to Professor Harry Berman of Harvard University for the loan of the cut illustrating the various silicon-oxygen structural types.

Doctors W. T. Schaller, Michael Fleischer, and R. C. Wells of the U. S. Geological Survey have reviewed the manuscript and made numerous suggestions which have improved the paper. The section on testing of mineral powders was largely contributed by Dr. Schaller. Dr. Fleischer had made a list of gelatinizing minerals in connection with his revision of Brush and Penfield's *Manual of Determinative Mineralogy*, and he carefully checked the list compiled by the writer. The generous help of his colleagues, however, in no way relieves the writer from full responsibility for any errors of fact or opinion that may be present.

[40] Gruner, J. W., *Am. Mineral.*, **21,** 449 (1936).

[41] Clarke, F. W., and Schneider, E. A., *Am. Jour. Sci.*, **40,** 303 (1890).

[42] Caillere, S., *Bull. soc. franc. mineral.*, **59,** 261 (1936).

MEASUREMENT OF THE THREE PRINCIPAL INDICES OF REFRACTION IN MICACEOUS MINERALS BY IMMERSION ON A TILTING STAGE

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Abstract

An accurate measurement of the refractive index for the vibration direction normal or nearly normal to the plane of cleavage in micaceous minerals is easily obtained by immersion measurements on a tilting stage. The simple theory of the method is developed and the application of the method to muscovite is described. Material from Mattawan township, Ontario, gave $\alpha=1.567$ (tilting method), 1.566_5 (total reflectometer, M. E. Jefferson), and by immersion on the horizontal stage, $\beta=1.606$, $\gamma=1.611$, in sodium light.

The micas and related platy minerals (brittle micas, chlorites, vermiculites) are pseudo-hexagonal in structure and form, and consequently pseudo-uniaxial in optical behaviour with the acute bisectrix nearly normal to the plane of eminent cleavage. The refractive indices for the two principal optical directions which are practically in the cleavage plane are conveniently measured by immersion on a horizontal stage; on the other hand the measurement of the refractive index for the third principal optical direction, which is nearly normal to the cleavage, is difficult, since it involves setting the plate on edge, and it is not likely to be very accurate, since the conditions are unfavourable for the Becke effect and the observation may have to be made very rapidly while the plate moves through the upright position.

In the course of a study of muscovite from a recently developed Canadian deposit one of us (R. B. F.) was faced with the problem of obtaining an accurate measurement of the index of refraction nearly normal to the cleavage. Noting that Jefferson (in Hendricks, 1939) had recently obtained measurements of this index on numerous micas using the total reflectometer, this method was tried, but the available instruments did not give good shadow-edges, even with the arrangements devised specially for muscovite by Viola (1900, p. 118). The problem was finally solved by making immersion measurements on a tilting stage, which gave us numerous consistent values for the desired principal index. Subsequently Dr. Jefferson was good enough to measure this index on our material using the total reflectometer. His result agrees with ours, showing that the tilting method gave the correct value. Since the method is also convenient and applicable to the wide range of platy minerals, the present account of the method and its application to muscovite may be of interest.

THEORY OF THE METHOD

Figure 1 represents a crystal cleavage place C, with greatly exaggerated thickness, mounted in an immersion medium I with refractive index ρ, between glass hemispheres GG with refractive index μ. We assume the special optical orientation which is almost realized in micaceous minerals, namely one principal vibration direction, in this case $OX=\alpha$, normal to the cleavage plate. The other two principal vibration directions, $OY=\beta$, and $OZ=\gamma$, are thus in the plane of the plate which has been arranged to tilt about OY which is normal to the plane of the drawing. The ellipse $XZX'Z'$ is a principal section of the indicatrix of the crystal. The value of γ is known from previous immersion measurement on the horizontal stage; α is to be found. The refractive index ρ of the liquid has been chosen less than γ and presumably greater than α. Vertically propagated polarized light enters at M and the system has been tilted from the horizontal HOH' through an angle i, in which position the apparent refractive index of the crystal plate equals ρ, the refractive index of the liquid.

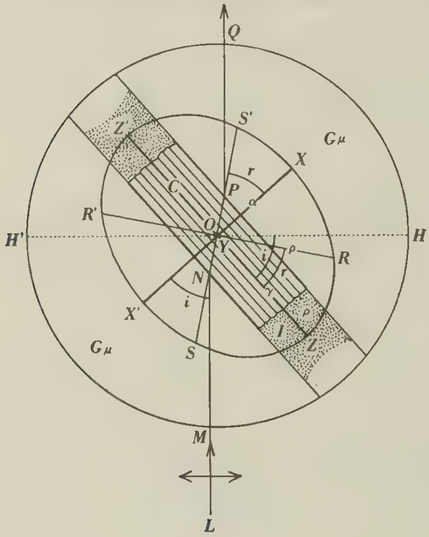

FIG. 1

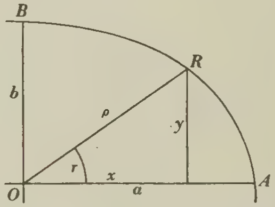

FIG. 2

In general, a radius of the indicatrix and the (rectangular) semi-axes of the normal central elliptic section give, respectively, the wave direction of light transmitted in a biaxial crystal and the two corresponding vibration directions and their refractive indices. In the present special case the direction of transmission is in the plane XOZ and we are concerned only with the vibrations in this plane. A beam of light L, polarized in the plane normal to HOH', passes into the lower hemisphere at M without refraction and enters the crystal plate at N with the angle of incidence i. Within the crystal plate the wave direction is NOP which is inclined to the plate normal at the angle of refraction r. At P the beam enters the upper hemisphere at the angle i, and leaves the system at Q with negligible refraction, if the crystal plate is thin compared to the radius of the glass sphere.

With reference to the section XOZ of the indicatrix, the wave direction is NOP or SOS', with the angle $XOS'=r$, and the vibration direction is ROR', with the angle $ZOR=r$. The apparent refractive index of the plate is ρ, and therefore OR, the refractive index associated with the wave-direction SOS', equals ρ. We may therefore write

$$\sin i : \sin r = \rho : \mu, \text{ or}$$

$$\sin r = (\mu \sin i)/\rho \qquad (1).$$

Thus r is obtained at once from the known values of μ, ρ, i, and we have the direction r and the length ρ of a radius of the ellipse whose major axis γ is known. Similar relations hold when OZ is taken as the tilting axis of the system.

Given one semi-axis of an ellipse, one radius, and the included angle, the other semi-axis is readily obtained from the equation of the ellipse. In Fig. 2 OA, OB, are the semi-axes of the ellipse with lengths a, b: R is the point x, y. We have

$$x^2/a^2 + y^2/b^2 = 1, \text{ or}$$

$$b^2 = y^2/(1-x^2/a^2).$$

Corresponding to Fig. 1, $a=\gamma$ (the known semi-axis), $b=\alpha$ (the unknown semi-axis), $OR=\rho$ (the determined radius), $x=\rho \cos r$, $y=\rho \sin r$. Substituting these values in the equation of the ellipse we obtain

$$\alpha^2 = (\gamma^2\rho^2 \sin^2 r)/(\gamma^2-\rho^2 \cos^2 r) \qquad (2),$$

or with OZ as the tilting axis

$$\alpha^2 = (\beta^2\rho^2 \sin^2 r)/(\beta^2-\rho^2 \cos^2 r) \qquad (2').$$

Thus each measurement of ρ and i (giving r), and the known γ or β, gives an independent value for the unknown α, and therefore a sufficient number of observations should yield a reliable average for the unknown refractive index.

The value of α having been determined in this way, it is of interest to compare the measured indices ρ with the calculated indices given by the experimental angle r together with α and γ or β. For this purpose equations (2) and (2′) may be rearranged to give

$$\rho^2=\alpha^2\gamma^2/(\alpha^2\cos^2 r+\gamma^2\sin^2 r) \tag{3}$$
$$\rho^2=\alpha^2\beta^2/(\alpha^2\cos^2 r+\beta^2\sin^2 r) \tag{3'}$$

Similarly, to compare the experimental angles r with the angles calculated from the indices ρ together with α and γ or β, we have

$$\cos^2 r=\gamma^2(\rho^2-\alpha^2)/\rho^2(\gamma^2-\alpha^2) \tag{4}$$
$$\cos^2 r=\beta^2(\rho^2-\alpha^2)/\rho^2(\beta^2-\alpha^2) \tag{4'}$$

APPLICATION OF THE METHOD TO MUSCOVITE

The tilting immersion method was applied to muscovite from Mattawan township, Ontario, which has been studied in some detail by one of us (R. B. F.) with a view to a fuller description to be given elsewhere. This material gives perfectly plane colourless cleavage sheets in which the angle between X (acute negative bisectrix) and the cleavage normal was found to be less than 1°, by exact measurement with a special device. The special optical orientation assumed in the theoretical section is thus practically attained. Careful measurements on the horizontal stage, with sodium light and a new set of immersion liquids, gave $\beta=1.606$, $\gamma=1.611$.

It was found that the best Becke effects were obtained on torn edges of thin sheets rather than on the straight ribbon edges given by separation along ($h0l$) glide planes. Such torn sheets were mounted between glass hemispheres with refractive index $\mu=1.554$ in liquids with refractive indices ρ ranging from 1.605 to 1.580 in steps of 0.005. The mounts were adjusted on the universal stage to bring first OY then OZ into the principal left-right axis of the stage. All the observations were made with the sodium vapour lamp and the polarizing nicol set to give light vibrating in the plane normal to the tilting axis. The angles of tilt, i, were read to the nearest half degree, the recorded values being averages of several readings taken with the plate tilted to the front and to the back. This procedure eliminated the small error introduced by the small inclination of X to the cleavage normal.

A plate mounted in this way in an oil of index ρ (between α and γ) shows in the horizontal position a strong Becke effect, mineral>liquid. On tilting the stage the Becke effect becomes weaker and at some angle of tilt the edge under observation vanishes. On further tilting of about 4° the edge reappears, giving the effect, mineral<liquid with increasing strength.

To determine more closely the angle of tilt at which the apparent index of the plate is equal to the index of the liquid, the stage was tilted to approximately the mid position of the invisible range and the angle of the revolving stage of the microscope was noted. This stage was then turned until the edge reappeared, in one direction and then in the other, and the readings were noted in each case. If necessary the tilt was changed until equal angles of rotation of the microscope stage, to the right and to the left, gave reappearances of the edge. When this condition was reached it was assumed that the correct angle of tilt had been found. In this way a series of measurements of i and ρ were made with OY and with OZ as the tilting axes.

Table 1 gives the refractive indices of the liquids used (ρ) and the observed angles of tilt (i), together with the angles of refraction (r) obtained by equation (1) and the values of the unknown index of refraction (α) given by equations (2) and (2′). The average value of α is 1.567. The extreme variation is $+0.005$ to -0.003, the largest variation occurring at the smallest tilt when, as might be expected, the measurement is least accurate. Between 30° and 50° of tilt the variation is ± 0.001 which is less than the limit of accuracy usually claimed for the immersion method.

To verify the value of α obtained by the tilting method we sent specimens of the mica to Dr. Merrill E. Jefferson who kindly tested a series of cleavage plates, including seven from the actual piece which we had used, on the total reflectometer. In his reply Dr. Jefferson stated that the best value he obtained for α was 1.566_5 which is practically identical with our value 1.567.

These independent observations show that the tilting immersion method gives results quite as accurate as those that can be obtained on a horizontal stage and that a single good observation at a tilting angle of about 45° will give a good value for the unknown index of refraction. Furthermore it will be noted in the table that i and r do not differ greatly even though ρ and μ differ considerably. If therefore the refractive indices of the liquid and the glass are nearly alike no considerable error will be introduced by assuming that r equals i.

Comparison of the Calculated and Experimental Values of ρ and r

Given the three refractive indices, α, β, γ, the value of ρ for a given value of r may be calculated from equations (3) and (3′), or the value of r for a given value of ρ may be obtained from equations (4) and (4′). The results of such calculations are given in Tables 2 and 3. From these we see that the greatest difference between the calculated and experi-

TABLE 1. REFRACTIVE INDEX α COMPUTED FROM IMMERSION MEASUREMENTS ON TILTED PLATES OF MUSCOVITE
($\beta=1.606$, $\gamma=1.611$, $\mu=1.554$)

	Tilting axis *OY*						
ρ	1.605	1.600	1.595	1.590	1.585	1.580	
i	23½°	31°	37°	44½°	50°	55°	
r	22°43′	30°01′	35°54′	43°14′	48°41′	53°41′	
α	1.572	1.568	1.566	1.567	1.566	1.564	Av. 1.567

	Tilting axis *OZ*					
ρ	1.600	1.595	1.590	1.585	1.580	
i	26°	32°	40°	46°	53°	
r	25°12′	31°05′	38°55′	44°51′	51°46′	
α	1.571	1.566	1.567	1.566	1.564	Av. 1.567

mental values of ρ is 0.002 while the mean difference is less than 0.001. The greatest difference between the calculated and experimental values of r, which is nearly equal to the tilting angle i, is nearly 3° while the mean difference is 1.3°. The same facts are expressed in Figs. 3 and 4 which give the graphs of equations (3) and (3′), respectively, and points corresponding to the experimental values of ρ and r.

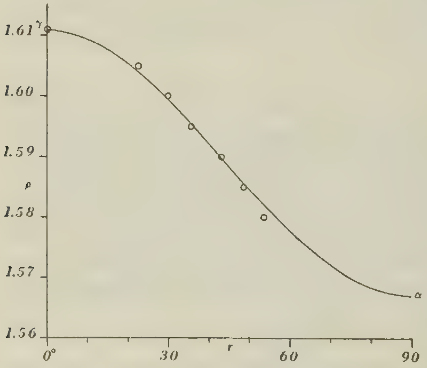

FIG. 3

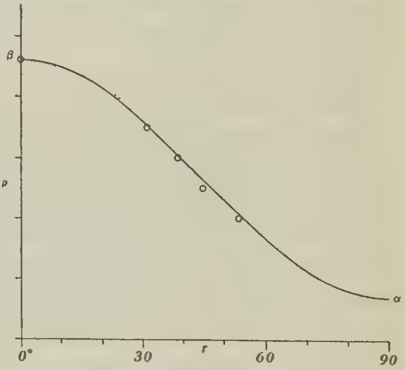

FIG. 4

SPECIALIZATION AND GENERALIZATION OF THE TILTING METHOD

The theory given for the tilting immersion method applies directly and strictly to orthorhombic crystals with cleavage parallel to any pinakoid and to monoclinic crystals with cleavage parallel to the symmetry plane. In the case of cubic crystals and uniaxial crystals with prismatic cleavage, n, ω, ϵ, are measured on the horizontal stage. In uniaxial crystals with basal cleavage ω is obtained on the horizontal stage and ϵ by tilting about any direction in the cleavage plane. In the case of monoclinic crystals with cleavage in the zone [010] the index of refraction for the vibration direction [010] is measured on the horizontal stage. If the plate is then set to tilt about [010] the orientation of the indicatrix is at once obtainable and two tilting immersion measurements

TABLE 2. CALCULATED AND MEASURED INDICES ρ AT THE EXPERIMENTAL ANGLES r
($\alpha=1.567$, $\beta=1.606$, $\gamma=1.611$)

	Tilting axis *OY*						
r exper.	22°43′	30°01′	35°54′	43°14′	48°41′	53°41′	
ρ calc.	1.6042	1.5997	1.5955	1.5899	1.5857	1.5820	
ρ exper.	1.605	1.600	1.595	1.590	1.585	1.580	
$\Delta\rho$	+0.0008	+0.0003	−0.0005	+0.0001	−0.0007	−0.0020	Av. 0.0007
	Tilting axis *OZ*						
r exper.	25°12′	31°05′	38°55′	44°51′	51°46′		
ρ calc.	1.5987	1.5953	1.5903	1.5862	1.5816		
ρ exper.	1.600	1.595	1.590	1.585	1.580		
$\Delta\rho$	+0.0013	−0.0003	−0.0003	−0.0012	−0.0016		Av. 0.0009

TABLE 3. CALCULATED AND EXPERIMENTAL ANGLES r AT THE MEASURED INDICES ρ
($\alpha=1.567$, $\beta=1.606$, $\gamma=1.611$)

	Tilting axis *OY*						
ρ	1.605	1.600	1.595	1.590	1.585	1.580	
r calc.	21°12′	29°31′	36°33′	43°07′	49°41′	56°33′	
r exper.	22°43′	30°01′	35°54′	43°14′	48°41′	53°41′	
Δr	+1°31′	+0°30′	−0°39′	+0°07′	−1°00′	−2°52′	Av. 1.1°
	Tilting axis *OZ*						
ρ	1.600	1.595	1.590	1.585	1.580		
r calc.	22°52′	31°43′	39°23′	46°42′	54°17′		
r exper.	25°12′	31°05′	38°55′	44°51′	51°46′		
Δr	+2°20′	−0°38′	−0°28′	−1°51′	−2°31′		Av. 1.5°

will suffice to determine the refractive indices for the two vibration directions in the symmetry plane.

The general case is presented by monoclinic crystals with prismatic cleavage and triclinic crystals with any cleavage. In such cases it will be seen that, by tilting about any principal axis of the indicatrix, three tilting immersion measurements will be needed to determine the lengths and orientation of the other two axes of the indicatrix. In practice the tilting immersion method is most likely to prove useful in the case of crystals with micaceous cleavage which is generally associated with a layer structure and pronounced uniaxial optical pseudo-symmetry.

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PEGMATITE CRYSTALLIZATION

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ABSTRACT

The authors try to analyze the geological, physical, and chemical conditions which control precipitation and growth of pegmatite minerals. The growth and persistence of large crystals is attributed as follows: (1) The great chemical complexity of the solutions, which reaches its climax in the last stages of magmatic differentiation; (2) establishment of temperature gradients along the pegmatite thorofares, both from place to place in the thorofares, and from them into the wall rock. The variation in these temperature gradients and in the speed of flow of solutions provides optimum conditions for replacement and crystal growth processes; (3) the tendency of certain crystals in suitable solutions to gain increased stability with increase in size.

INTRODUCTION

In a study of pegmatite crystallization the most important aspects deal with the nature of the fluids which build the pegmatite, temperature considerations, replacement, and conditions favoring the formation of large crystals which are uniquely characteristic of pegmatites. Following the reasoning of Fersmann[1] and others, the pegmatite-forming process will be considered for the majority of cases as a one-stage affair.

Systems of various rock components have been prepared synthetically and studied by others, and the results of such studies furnish indisputable data as to the behavior of hypothetical magmas not complicated by the presence of the minor constituents characteristic of actual magmas. However, as a magma crystallizes, the constituents present in minor amount, being far from saturation, tend to accumulate in the mother liquor, unless they are coerced into precipitation with the great mass of essential rock minerals (such as the association of some titanium, zirconium, and hafnium with silicon in silicates). The mother liquor is thus changing gradually in character with respect to the minor constituents, and by the time pegmatite formation has become well established, the mother liquor is quite different from the original mass; consequently, the "mass production" methods of common igneous rock formation may not apply closely in most cases to pegmatites.

NATURE OF PEGMATITE FORMING SOLUTIONS

Pegmatites differ from igneous rocks in several respects, the most important being the accumulation of certain rare elements in the pegmatite. These rare elements, in general, are not widely diffused and never characteristic of the so-called parent rock. This difference in composition between pegmatite and parent rock must be the result of a process of rare element concentration whereby, in general, the rare elements are not precipitated with the bulk of the rock-forming material, but are reserved in the mother liquor. During the formation of the parent rock, the rare elements represent minor constituents of the magma, with reference to which it is unsaturated. Consequently they are not precipitated. On the other hand, the magma is saturated with respect to the rock-forming components. As a result of the crystallization of the parent rock, the mother liquor changes progressively. It begins as a solution dominantly rich in the essential rock-forming components, and of an apparently simple composition. This apparent simplicity is due to the very small proportion of accessory constituents. The mother liquor finally becomes highly complex, containing as essentials many constituents which ordinarily are merely accessory, including certain very scarce elements, which usually are not recognized at all in igneous rocks.[2] Finally, then, enrichment with respect to the rare elements and the minor rock-forming components is accomplished and their precipitation becomes possible.

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[1] Fersmann, A., Über die geochemisch-genetische Klassification der Granitpegmatite: *Mineral und Petrog. Mitteilungen*, **41**, 64 (1931).

Thus we have a solution whose solvent power depends upon nearly every one of the components originally present in the parent magma. During the formation of the parent rock, the solvent power had been determined overwhelmingly by a limited group of rock-forming constituents; in the pegmatite stage, however, the solvent power increased in versatility as a result of the complexity of the resultant mother liquor. This complexity probably contributes to the formation of large crystals, and may be an important factor in replacement.

Other materials besides the rare elements accumulate in the mother liquor. These are the most volatile and the most soluble components of the magma, and they are important in determining the physical character and the chemical properties of the mother liquor. Water, and compounds of fluorine are most prominent in this connection. Such compounds as the fluosilicates and fluosilicic acid, and fluorides such as fluorite, are excellent fluxes and cause the mother liquor to become more fluid.

Minerals will be formed from such solutions by one or more of several changes, all of which must result in saturation of the solution with respect to the mineral components before precipitation can occur. These are as follows:

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[2] Fersmann (*ibid.*, p. 205) points out that most pegmatites carry about twenty-five different minerals; the Norwegian pegmatites are exceptional with about seventy-five. Most igneous rocks contain less than ten different minerals; of course the number of different minerals indicates the relative complexity of the parent solutions.

(1) Lowering of temperature. This is the most important change leading to mineral formation.
(2) Escape of part or all of the volatile solvents or precipitation of a mineral involving the solvent.
(3) Saturation of the mother liquor with a particular component due to solution of country rock, or of previously formed pegmatite material. In these cases, ordinary pegmatite minerals would be formed nearer the source of mother liquor than normally; new minerals may be formed by the reaction of pegmatite fluids with the wall rock, as in the formation of andalusite in contact rocks.

For minerals to precipitate, it is immaterial whether the solution be "dilute" or "concentrated," but in any case, the solution must be saturated. The terms "dilute" and "concentrated" have no meaning in this connection because they are purely relative—a solution can be dilute and still be saturated.

Re-solution of previously formed minerals can take place whenever the mother liquor is unsaturated toward them. Nevertheless, a substance which precipitates may thereafter be prevailingly insoluble in the same solvent, even though the solvent later becomes unsaturated with reference to it; this insolubility probably accounts for many mineralogical phenomena, as will be pointed out later.

Temperature Considerations

We must assume that the major part of pegmatite formation immediately follows the solidification of the parent rock,[3] and that cracks or openings suitable for pegmatite development form in the parent rock and in the country rock. Certain residual liquors result from the formation of the parent rock. The mouths of the cracks will necessarily be at the temperature of the original mother liquor, and as this residual liquor is forced into the cracks, temperature gradients will be established both along the stream of pegmatite flow and transverse to it into the country rock. Cooling will necessarily be slow because the cracks pass through hot country rock previously heated by conduction, diffusion, etc., from the parent magma. The rate of cooling of the pegmatite-forming fluids depends for one thing upon the cooling rate of the country rock traversed by the cracks. Since the country rock cools slowly, the cracks maintain a low temperature gradient, and the passing fluids must also cool slowly. The moving pegmatite fluids normally will be at a higher temperature than the crack walls, provided the flow of fluid is essentially uniform; if the flow is not uniform, for a time there may be regions where the fluid temperature drops to the wall rock temperature. Necessarily, the general direction of pegmatite flow will be the direction of lowering temperature. The temperature gradient, in association with other factors, will then determine the distribution of the pegmatite minerals.

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[3] Frank L. Hess has interpreted the introduction of spodumene into North Carolina pegmatites as being considerably later than the formation of earlier pegmatite material, partly dependent upon and localized by diastrophic movements. *Cf.* Spodumene pegmatites of North Carolina, *Econ. Geol.*, **35**, 950 (1940).

The slow rate of cooling of the pegmatite zone will favor the growth of large crystals, but it is evident that the large crystals characteristic of pegmatites cannot be accounted for entirely by this slow rate of cooling. Certainly a much slower and more uniform cooling rate existed in the central regions of the parent rock during its formation, but extremely large crystals are not found there.

The Pegmatite Thorofare

We suggest that the space of pegmatite formation be called a "pegmatite thorofare." The pegmatite process may be considered as a one-stage affair; that is, *ideally there is a single major injection of magmatic mother liquor into the pegmatite thorofare which continues until the supply of mother liquor is exhausted.* Naturally, the ideal case is rare. In many cases, what may be considered the normal course of procedure is interrupted by diastrophism or other geological events which have no necessary connection with the pegmatite process. In such cases, there may be either an interrupted and later renewed injection of pegmatite fluids or the whole process may be permanently cut short along any one thorofare under consideration, and the end stages of injection may be bypassed through entirely different thorofares. Consequently any particular pegmatite vein may represent any or all parts of the pegmatite sequence. Perhaps a pegmatite which represents within itself all significant changes in the mother liquors in chronological relations is as rare as an outcrop which shows a continuous stratigraphic sequence from Cambrian to late Permian.

Considering the high temperatures and pressures in operation, and the very high mobility of the pegmatite solutions (especially those termed "pneumatolytic"), the thorofares may range in size from skeins of sub-microscopic spaces to open cracks yards wide.

As the mother liquor travels through the pegmatite thorofare, the pegmatite minerals are precipitated individually, as saturation is reached at definite temperatures. At the same time, solution of pegmatite minerals or country rock may take place at any point followed by precipitation of these dissolved materials at some point of lower temperature—that is, generally at a place farther from the source of mother liquor (provided the flow is essentially uniform); this is replacement. Thus there is a process of precipitation which may be accompanied by solution while the pegmatite fluids are flowing essentially in a one-way direction through the pegmatite thorofare. This may be likened to a process of unloading and loading at various stations along a transportation system or thorofare, for actually, the pegmatite fluid is the medium of transport of pegmatite constituents.

The speed of flow will vary from place to place along the thorofare, being slow at places of easy or wide passage, and rapid in constrictions or in places of reduced permeability. Supposing the wall rock to have the same temperature at two places, one of narrow passage, and the other of large cross section, then the fluid will pass swiftly through the narrow places and slowly in the large openings. The swift flow will carry high temperatures farther down the thorofare than the slow stream can. Consequently, the temperature gradient between fluid and wall rock along the thorofare increases in places of fast flow and drops definitely at places of slow movement. At the down-stream part of a constricted passage, there should be an unusually high temperature gradient between fluid and wall rock. We might expect free precipitation and selective solution, or abundant replacement, at the upstream side of the wide spaces in pegmatite thorofares, where there would naturally be a sharp drop in the temperature gradient between the pegmatite fluid and the wall rock.

Inasmuch as narrow passageways increase the relative area of heat conduction from passing solutions into the walls of country rock, there must be limiting conditions under which very fast small streams of fluid would cool so rapidly that the temperature gradient down stream would fall more rapidly than in places where the channels are large in cross sectional area and the fluids move slowly. A balance tends to be established, of course, between the temperature of the passing fluids, the surface of the thorofare, and the temperature gradient from the surface into the country rock. Consequently, suggestions as to places of steep temperature gradient must be very general in application.

In cases such that the parent magma supplies pegmatite fluids under varying pressures, then the speed of flow at any one place will vary from time to time. Such variation in the speed of flow again causes a change in the physical chemical regime of the whole pegmatite thorofare. When the speed of supply increases, the temperature of the fluid at any given point must rise, and the temperature gradient between fluid and wall rock or early pegmatite crystals must increase, and *vice versa.* For these and probably other reasons, there can hardly be much uniformity in physical chemical conditions at any point along a pegmatite thorofare for very long. Whenever there is a rapid temperature change, it causes alternation between solution and precipitation at crystalline surfaces, thus promoting the process of replacement.

Supposing the country rock to be affected by diastrophism, then the existent pegmatites may be either crushed into increased compactness, or shattered into open cracks. In either case the speed of flow of pegmatite liquors will change, thereby tending to increase or reverse the existing processes of deposition or replacement. In certain areas, fracturing is known to have been of primary importance in pegmatite mineralization.[4]

Variation in the speed of flow of pegmatite fluids may result in replacement. When temperatures become higher at the surface of a crystal (or at the wall rock), the mother liquor may become unsaturated toward the material, depending on its composition and the period of its formation in the pegmatite process. This unsaturation will result in solution of the material provided the latter is not passive towards the solvent. As solution proceeds, the material will be replaced by higher temperature minerals which ordinarily would precipitate at a place nearer the source of mother liquor. In other words, where the speed of flow increases the temperature difference between fluid and wall rock, or earlier pegmatite crystals, increases. Then materials, with reference to which the solvent is far from saturation, may dissolve freely; but at the same time the fluid, constantly cooling as it flows to regions of lower temperature, is precipitating the common rock-forming minerals (at least) with reference to which the fluid is saturated. Such a condition of selective solution and compulsory precipitation is favorable to replacement.

Where the speed of flow decreases, the temperature difference between wall rock and solvent is low, and solution of solids is at a minimum. However, as in all other cases, the fluids are actually cooling as they flow and therefore are constantly renewing the tendency to precipitate. The result is that where fluids flow slowly there is a general tendency for precipitation without solution, effecting ordinary crystallization without replacement. When the fluids maintain a constant speed of movement, a general balance between supply and precipitation becomes established, and proceeds so long as this flow continues and space for crystal growth remains. This is represented in nature by the common high-temperature granite pegmatites.

Figure 1 is designed to illustrate in a general way the distribution of solution, precipitation, and replacement along a thorofare as a result of differences in cross-sectional area of the space available for the flow of fluids, and corresponding variations in the speed of flow of the passing solutions.

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[4] Hess, Frank L., The spodumene pegmatites of North Carolina: *Econ. Geol.*, **35**, 942–966 (1940); Hess, Frank L., Whitney, R. S., Trelithen, J., and Slavin, M., The rare alkalis in New England: *U. S. Bur. Mines, I. C.* **7232**, 8–10 (Jan., 1943).

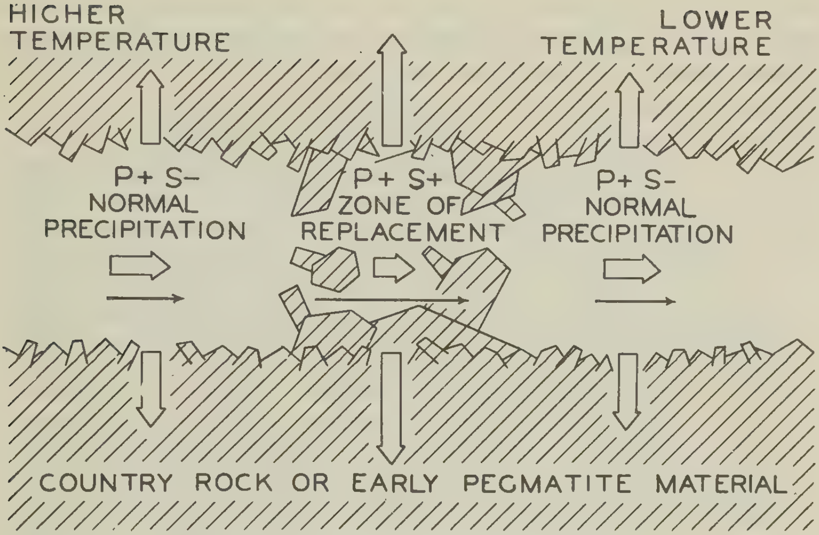

Fig. 1. Diagram to illustrate relations of precipitation, solution and replacement with the temperature gradients along a pegmatite thorofare.

Solid arrows indicate direction and relative speed of flow. Length of hollow arrows indicates relative intensity of temperature gradients. P+ stands for precipitation. S, + or −, stands for important or negligible solution, respectively.

Formation of Large Crystals

The very coarse crystallization of pegmatites is unique in that it is found in no other naturally occurring aggregate of minerals. One of the most important factors which is necessary for large crystal formation is a steady, uniform supply, or else a repeatedly renewed supply, of material to the growing crystal. This may be accomplished by lowering the temperature of a system of solvent and solute, wherein the solvent is saturated and the solubility of the solute decreases with lowering temperature. Another process would involve a decrease in the amount of solvent, such as one of the common rock-forming minerals in the case of a magma. Precipitation may be increased also by an actual mechanical removal of the solvent, due to diastrophic or irruptive processes. Such processes must account in part for large crystals in pegmatites, but there must be other factors operative. Certainly a steady, uniform supply of material is not all that is necessary for large crystal development. This must be so because we do not find very large crystals in the centers of igneous intrusions wherein the conditions of crystallization (slow cooling particularly) were certainly more uniform than in a pegmatite, and where there was an abundance of material available from solution. This at once indicates that pegmatites are formed under conditions materially different from those controlling igneous rock formation.

From the data based on more than three hundred pegmatites, given by Fersmann,[5] several important points may be presented:

(1) In the epimagmatic zone (800°–700°), the structure is generally aplitic or graphic. Very large crystals are not characteristic. The rarer minerals found here, such as monazite, garnet, zircon, titanite, etc., may be considered to have precipitated by virtue of their limited solubility in the cooling mother liquors. Quartz is often abundant. In the epimagmatic stage of pegmatite formation, the mother liquor may be considered still to be essentially simple in composition, and the common rock-forming components[6] are still crystallizing in much the same manner as in the parent rock.

(2) The pneumatolytic-pegmatoidal zone (600°–400°) is characterized by the large crystals of pegmatites, and in its later stages by a variety of complex minerals. The complexity of the pegmatite minerals found here indicates that the parent mother liquor itself had been complex, most of the abundant igneous rock-forming components having crystallized during the epimagmatic and early pneumatolytic stages. It is important to recognize also that the pneumatolytic zone is the characteristic place in the pegmatite where the very large crystals are found. These facts immediately suggest that the formation of large pegmatite crystals is intimately connected with the complex nature of the solvent.

(3) A characteristic feature of the hydrothermal zone (400°–50°) is the precipitation of fluorine compounds such as apatite, cryolite, and fluorite from the remaining complex solvent. The precipitation of silica is more pronounced in the hydrothermal zone than in the late pneumatolytic-pegmatoidal zone.

(4) An inescapable observation regarding large pegmatite crystals is the fact that they are all silicates. The preponderance of silicates indicates something as to the nature of the solvent. We may conclude at least that the pegmatite mother liquor which eventually leads to minerals characteristic of the hydrothermal zone not only must be an excellent solvent for silicates, but must be high in fluorine compounds. This is supported by the fact that the precipitation of silica is negligible in the late pneumatolytic stage where fluorine compounds constitute an effective proportion of the mother liquor; following the precipitation of fluorine compounds, however, in the hydrothermal zone, the silica is also precipitated. Apparently the silica is held in solution by fluorine compounds. In the pneumatolytic stage, these fluorine compounds, such as fluosilicic acid, in addition to acting as solvents for silicates, must have promoted the fluidity[7] of the mother liquor. Apparently this combination of fluidity and high solvent power promotes the growth of large silicate crystals.

It is a well known fact that large crystals of a mineral are less susceptible to chemical treatment and to solution, in general, than are small crystals or amorphous forms of the same mineral. *The mere size of pegmatite crystals encourages their persistence at least, and probably promotes their growth.* It was pointed out earlier that a substance once precipitated may thereafter be insoluble in its solvent even though the solvent later becomes unsaturated with respect to it. It is probable that large pegmatite crystals represent such a case. Once such a crystal has formed, it will be more or less passive toward resolution as a result of changing conditions in the pegmatite thorofare, but in later periods of precipitation it may resume its crystallization. This would permit the crystal periodically to increase in size, without suffering corresponding periods of wastage. The zoning often observed in large pegmatite crystals probably is due to such a process—the material crystallizing after a discontinuance of precipitation in some cases being of a slightly different, but analogous composition.

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[5] *Loc. cit.*, pp. 64–83.

[6] The writers do not recognize the euhedral habit of zircon, titanite, and monazite necessarily to indicate early crystallization in an igneous rock any more than in the case of garnet, which is universally recognized as metacrystic.

[7] By promoting fluidity, the writers mean that the solution becomes more mobile, and the movement of ions, atoms, and molecules is promoted.

In order to promote large crystal growth in a simple solvent it is possible that a condition of infinitesimal alternation between wastage and crystallization must be provided. H. C. Kremers[8] has postulated the same sort of theory to explain the growth of synthetic single optical crystals from the fused state. There is probably a region, perhaps scarcely more than a surface, of alternation in which impurities remain in solution and the pure material deposits in its proper place in the crystal lattice.

Such crystal growth must not be confused with that of large crystals growing at the expense of small ones, which is a matter of low ratio of surface to mass. This may also be pertinent to the problem of large crystals in pegmatites. It is a fact that renewed precipitation in pegmatites commonly takes place on crystals already well grown, and rarely in the form of a new generation of microlites. Consequently large crystals maintain their identity and increase in size, whereas microlites cannot persist.

No one of these conditions alone is responsible for large crystal growth in pegmatites. It seems to require a combination of special processes and conditions. These special features appear to be in the main:

(1) A constantly and/or repeatedly renewed stream of magmatic mother liquors.
(2) A persistently dropping temperature.
(3) Restriction of flow of the mother liquors into definite thorofares which in the generalized case are operative for a long time.
(4) A progressive complexity and chemical versatility of solutions.
(5) The presence of active solvents and fluxes for silicates.
(6) Conditions causing variations in the speed of flow along the thorofare, both from place to place and from time to time.
(7) Other conditions promoting selective solution and precipitation, regrowth, and replacement.

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[8] Personal communication from H. C. Kremers of the Harshaw Chemical Company, Cleveland, Ohio.

(8) The persistence of certain minerals beyond their expected conditions of stability.
(9) The increase in stability of certain crystals with the attainment of great size.

CONCLUSION

It is probably impossible to find any pegmatite or group of pegmatites in the same igneous suite which illustrates clearly all phases and all varieties of the better known mineralogical, textural, and structural features characteristic of pegmatites. Nevertheless, there appears clearly to be a gradational relationship between various types of pegmatites. It does not seem reasonable to expect to find all mineralogical variations in the same igneous suite, because each magma has its own assortment of constituent elements peculiar to itself. The resultant pegmatite of course cannot provide minerals composed of elements which are not represented adequately in the parent magma. There will always be differences in members of the same class of pegmatites derived from different magmas. Uniformity is not to be expected.[9] General accordance to type, however, seems to persist. The types represented in all parts of the world appear to show a coherent, progressive relationship, type to type, in spite of irregularities and hiati in any local aggregate of pegmatites. The process of pegmatite crystallization, like the cycle of erosion has its interruptions and its rejuvenations.

The conditions which compel the formation of large crystals in pegmatites are complex and probably are mutually coordinating in their effects. They appear to be most effective at temperatures definitely lower than those of igneous rock formation. The pegmatite solutions are extremely complex in composition, and correspondingly versatile in their activities. They are relatively enriched in silicate fluxes and in pneumatolytic components. The crystals once formed tend to persist in spite of potential solution, and to gain stability with increase in size. Variations in the flow of solutions affect the temperature gradients and thus promote selective replacement and enlargement of certain crystals.

Among all pegmatites of the pneumatolytic-pegmatoidal zone, no other feature displays such persistence as coarse crystallization, and perhaps the development of very large crystals requires a group of mutually augmenting conditions which constitutes the most nearly universal characteristic of pegmatites.

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[9] Cf. Hess, *et. al.*, *loc. cit.*, p. 10.

TWO ANDALUSITE PEGMATITES FROM RIVERSIDE COUNTY, CALIFORNIA

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Abstract

Reported occurrences of andalusite in pegmatite are reviewed and two new occurrences are described in which andalusite, corundum, microcline, and quartz are found in giant intergrowths, in metamorphic terrains. The geological setting is discussed and suggestions are offered as to the genesis of the occurrences. Thermal metamorphism of aluminous sediments and metamorphic differentiation are thought to account for the features of the two occurrences.

Introduction

Two pegmatite dikes, locally rich in andalusite, have been found in Riverside County, California. One dike containing giant crystals of andalusite is in Coahuila Mountain, an elongate foothill ridge of granitic peaks sub-parallel to the San Jacinto Mountains. The second locality is in an isolated hill standing above the Hemet Plain, near Winchester, California. The mineralogy, occurrence, and relations of the andalusite-bearing dikes to adjacent pegmatites are discussed.

Pegmatitic andalusite has been described from few localities, but it must be commoner than reports indicate, at least in some districts. The occurrences here discussed increase to five the known occurrences of andalusite in the pegmatites of this petrologic province;[1] two more, presumably from pegmatites, have been mentioned.[2] A few other occurrences have been reported.[3]

COAHUILA MOUNTAIN AREA

SKETCH OF THE REGIONAL GEOLOGY

Coahuila Mountain parallels the larger San Jacinto Mountains along their west base. It is separated from the San Jacinto by a major fault zone, containing, according to Fraser,[4] two major faults, the San Jacinto and Bautista. The oldest rocks in the block are a metasedimentary banded gneiss, mica schist, and marble. Hornblende gabbros with many porphyritic facies have invaded these rocks, and form small stock-like bodies in Coahuila Mountain, and batholithic masses to the southeast.[5] Later, granitic magmas extensively enveloped and transgressed the metamorphic and gabbroic rocks, and produced batholithic units that vary in composition from granite to quartz diorite. These are presumed to be of Jurassic age. These formational units and the geology of the entire San Jacinto quadrangle are described in Fraser's report.

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[1] Reported in a pegmatite from magnesite quarry near Winchester, 3 miles from Winchester locality herein described (Murdoch, Joseph, Andalusite in pegmatite: *Am. Mineral.*, **21**, 68–69 (1936); from a newly prospected pegmatite in T. 11 S., R. 3 W., Sec. 9, San Luis Rey quadrangle, near Vista, San Diego County, identified by the writer; and from the Jurupa Mountains, Riverside County, found by Mr. Melvin Swinney of Pomona College (personal communication from Professor A. O. Woodford of Pomona College).

[2] Kunz, George F., Gems, Jewelers' Materials, and Ornamental Stones of California: *Calif. State Min. Bur., Bull.* **37**, 99 (1905); it may be that the andalusite reported from Coahuila is from the same locality as the occurrence here described, but since Kunz gives no description or exact location, this cannot be verified. Dr. W. T. Schaller informed the writer by letter (March 14, 1941) that he had found pink andalusite in the Pala View Claim at Pala, California.

[3] Hess, Frank L., The natural history of the pegmatites: *Eng. Min. Jour. Pr.*, **128**, 289 (1925); Macdonald, G. A., and Merriam, Richard, Andalusite in pegmatite from Fresno County, California: *Am. Mineral.*, **23**, 588–594 (1938). Several localities are listed in Hills, E. S., Andalusite and sillimanite in uncontaminated igneous rocks: *Geol. Mag.*, **75**, 300 (1938).

[4] Fraser, Donald M., Geology of San Jacinto quadrangle south of San Gorgonio Pass: *Calif. Bur. Mines*, State Mineralogist Report, **27**, 518–519 (1931).

[5] Miller, F. S., Petrology of the San Marcos gabbro, southern California: *Bull. Geol. Soc. Am.*, **48**, 1399 (1937).

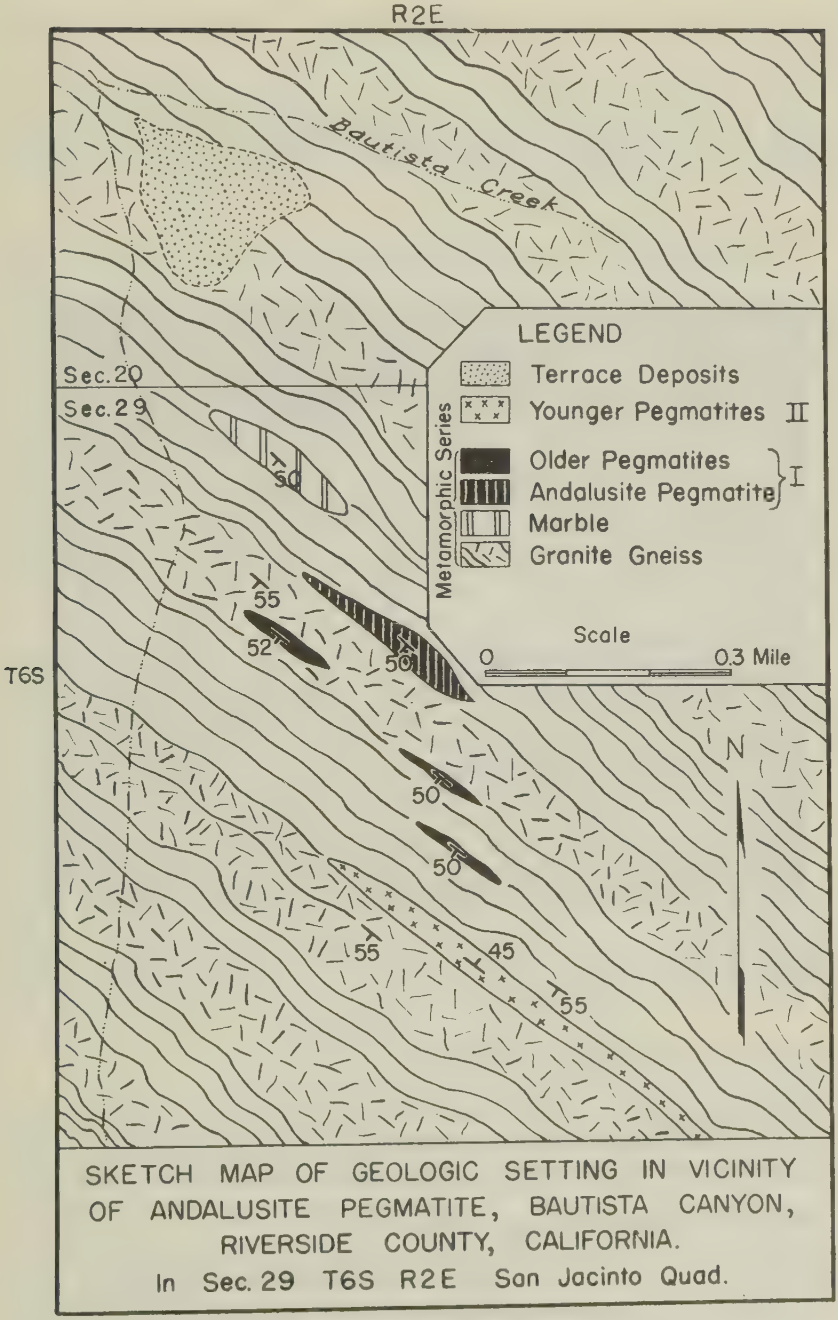
R2E
T6S
Bautista Creek
Sec. 20
Sec. 29
50
55
52
50
50
50
55
45
55
LEGEND
Terrace Deposits
Younger Pegmatites II
Older Pegmatites
Andalusite Pegmatite
I
Marble
Granite Gneiss
Metamorphic Series
Scale
0
0.3 Mile
N
SKETCH MAP OF GEOLOGIC SETTING IN VICINITY OF ANDALUSITE PEGMATITE, BAUTISTA CANYON, RIVERSIDE COUNTY, CALIFORNIA.
In Sec. 29 T6S R2E San Jacinto Quad.

FIG. 1

GEOLOGICAL RELATIONS OF THE PEGMATITES

General Statement

Two groups of pegmatites occur in the Coahuila area. They are believed to be genetically separate because of differences in spacial, structural, and mineralogical relations.

Pegmatites of Group I

The first group, less prominent and less extensive than those of group II, is associated with the metamorphic series, chiefly in gneissic rocks. Many of these pegmatites are lenticular, augen-like masses, parallel to the gneissic banding. They change abruptly in thickness along the strike of the gneissic zones; many terminate in a few dozen feet, reappear, and continue on the same strike. All those observed conform with the structure of the metamorphic rocks and to a regional strike of N. 45°–55° W., and regional dip of 45°–55° S. They range from a few inches to eight feet in width, and in the few exposed vertical sections show little persistence downward. The andalusite-bearing pegmatite is one in this group.

Pegmatites of Group II

The pegmatites of the second group cut rocks as young as the granitic intrusive with which they are associated in origin. Many dikes are found in the granodiorite, some in the gabbro, and some transgress the regional structure of the metamorphic series. The pegmatites of this group have greater linear persistence, often continuing unbroken along their strikes for a half mile or more. Dikes range from six inches to twenty-five feet in thickness, and are more constant in thickness along the strike than those of group I. Some of these pegmatites may be traced directly into the parent granitic body. This granitic massif is one of the widespread granitic intrusives of southern California,[6] with which pegmatites are associated in many other California areas.[7]

MINERALOGY OF THE PEGMATITES

Group I

General Mineralogy. In the comparatively few pegmatites in the metamorphic series, the normal quartz-microcline association is every-where present together with schorlite, biotite, and muscovite. Other minerals are rare, except that large pink and white andalusite crystals abound in one large pegmatite in sec. 29, T. 6 S., R. 2 E. (San Jacinto Quadrangle).[8] Shattered masses of translucent white, iron-stained quartz enclose large microcline and schorlite crystals, and giant bundles of pink and white andalusite. These grow in clusters in the quartz. Muscovite plates occur on faces of the andalusite and tourmaline, and as small books elsewhere in the dike. A little corundum occurs in the andalusite.

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[6] Reed, R. D., *Geology of California*, 96 (**1933**).

[7] Schaller, W. T., The genesis of lithium pegmatites: *Am. Jour. Sci.*, (5) **10**, 269–279 (1925); Rogers, A. F., Minerals from the pegmatite veins of Rincon, San Diego Co., Cal.: *School Mines Quart.*, **32**, 398–404 (1911); Schaller, W. T., Dumortierite: *Am. Jour. Sci.* (4), **19**, 211–224 (1905); *U. S. Geol. Surv., Bull.* **262**, 96–102 (1905); and others.

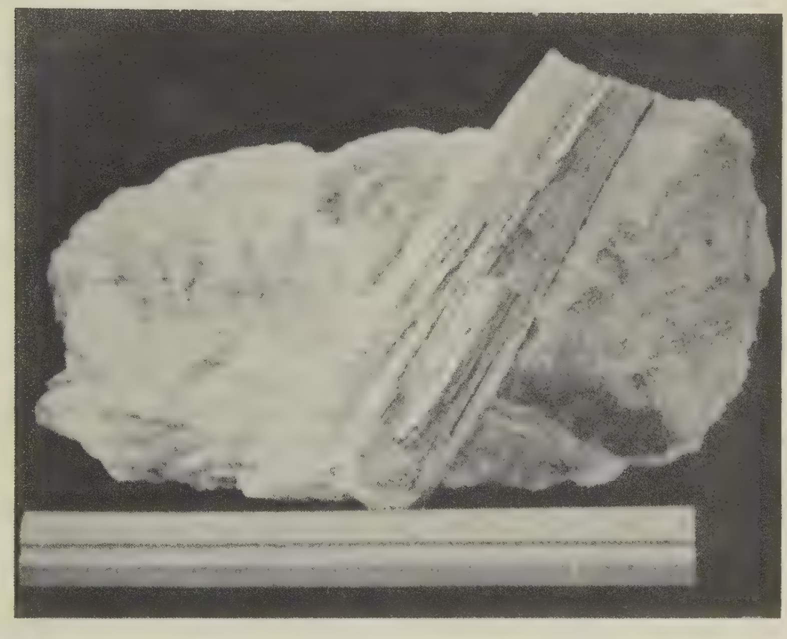

FIG. 2. Giant andalusite crystal in shattered quartz matrix. Note the similarity between this and the tourmaline form; there is no evidence, however, that andalusite is pseudomorphous after tourmaline. From Coahuila Mountain.

Andalusite. The andalusite occurs predominantly in local, wide zones in the pegmatite, as bundles of prismatic crystals in parallel and subparallel intergrowths. The bundles commonly range from two to five inches in thickness, and from six to fifteen inches in length. These exceptionally large groups are pink or brownish-pink, or shades thereof. Andalusite also occurs sparsely as rosettes and small radiating masses of white crystals in pockets in the dike, and along faces and contacts with microcline. In many places the two habits are closely associated.

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[8] Briefly described by Funk, B. Gordon, The sillimanite minerals: A summary: *The Mineralogist*, **8**, 131 (1940).

The andalusite of the first type shows pronounced color variation. In prismatic section, and commonly in the same individual, X varies from pale flesh-pink to colorless, and rarely to deep brownish-pink. The color changes are gradational in most specimens, but some crystals show sharp lines of demarcation between two sections with strong pleochroic contrasts.[9] Color zones are elongated parallel to c, but in some cases they transgress the elongation. Some basal sections show a pale flesh-pink to colorless pleochroism for Y and Z. Iron oxide stains were noted in the areas of pink pleochroism, but were absent in the colorless areas. In a recent paper,[10] the pleochroic variation in X was shown to be partly, if not entirely, due to variation in ferric iron content, present as an impurity in the andalusite.

Other Minerals. Large muscovite flakes coat the faces of individual prisms in the andalusite bundles; they also occur inside the crystals where some flakes are oriented parallel to the c axis, but mostly normal to it. Muscovite also occupies fracture and cleavage planes in the andalusite, commonly with its cleavage parallel to the planes of fracture or cleavage of the andalusite. This relation was noted in the andalusite from Fresno County.[11]

Where muscovite is abundant, nests of muscovite enclosed by andalusite contain small anhedral to subhedral grains of corundum. Most of these show the intense blue color of sapphire, some are colorless, and some are pleochroic with ϵ various shades of blue and ω colorless. Muscovite nests filled with granules of corundum are apparently common in andalusite deposits.[12] A few grains of corundum are in direct contact with the andalusite.

The andalusite shows prominent alteration rims of sericite from $\frac{1}{4}$ to $\frac{3}{4}$ inch thick. The sericite is compact, fine grained, and commonly surrounds muscovite flakes. Such sericitic rims are prominent on andalusite from most areas.[13] An exception is the occurrence at Winchester (see below).

Microcline perthite is abundant. It occurs in imperfect crystals ranging from a few inches in prism dimension to $1\times1\times3$ feet. The larger crystals are the commoner. They show the prism zones well developed, with some terminations. In many places the microcline is shattered.

Large schorl-tourmaline crystals interfinger all other minerals. Many are single crystals, with well developed terminations. The crystals vary from an inch to five inches in diameter, and from six to sixteen inches in length. Microscopically they show no unusual features. Many are bent and fractured.

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[9] Macdonald and Merriam, *op. cit.*, p. 589.

[10] Macdonald and Merriam, *op. cit.*, p. 592.

[11] *Ibid.*, p. 589.

[12] Kerr, Paul F., Andalusite and related minerals at White Mountain, California: *Econ. Geol* **27,** 625 (1932); Macdonald and Merriam, *op. cit.*, p. 589.

[13] Kerr, *op. cit.*, p. 635; Macdonald and Merriam, *op. cit.*, p. 589.

Group II

General Mineralogy. Pegmatite dikes of the second group are numerous. Most of them lie within the granodiorite and contain fairly simple and common pegmatitic minerals: microcline, quartz, schorlite, hessonite, muscovite, and biotite, in the usual giant texture relations. Graphic granite is rare. Rose quartz occurs in exceptionally well-colored, large, translucent masses, with some smoky quartz, hard jet-black schorlite crystals (up to three feet long), and occasional beryl. Some microcline has been produced commercially from a particularly wide dike in Sec. 22, T. 7 S., R. 2 E.

Cream-white microcline perthite is the most abundant mineral; albite is rare except in perthitic intergrowths. The microcline is subhedral and forms large aggregates, many of which show uniform cleavage trends over areas two or three feet square.

Two varieties of quartz are common: normal milk-white to colorless, and rose quartz. Masses of rose quartz 25 to 50 feet in two dimensions are common. Fracturing is slight, in contrast with much California rose quartz, and unbroken masses are obtainable.

The jet-black schorlite is massive and abundant in all dikes. Crystals from ten to forty inches long, in subparallel bundles, occur in white quartz and microcline in a very large dike in Sec. 30, T. 6 S., R. 2 E. Muscovite, biotite, or both, occur in all of the dikes, with muscovite predominant. Most of the tourmaline-rich dikes lack biotite. Beryl, in small yellowish-green crystals, was found in one dike. Biotite is commonly arranged along cleavages and fractures in the quartz and microcline, the biotite plates often arranged normal to the dike walls and marginal thereto.

EVIDENCE FOR TWO GENERATIONS OF PEGMATITES IN THE COAHUILA AREA

The two groups of pegmatites of the Coahuila area differ sufficiently to suggest that they may be genetically separate. This suggestion is based on the following evidence:

Space relations: (1) The dikes of the first group are confined to the metamorphic terrain; those of the second occur in all the rocks of the area and are especially numerous in the granitic formations. (2) The dikes of the first group conform with the regional structure of the gneisses; those of the second, though not observed to cut the first set, have strikes parallel, but dip nearly normal to the dip of the first group (see Fig. 1). (3) The habits of the dikes of the two groups differ notably; those of group I are interrupted, lenticular, and short; those of group II are tabular and persistent.

Internal structural relations and mineralogical contrasts: (1) Lack of oriented minerals in dikes of group I, compared to marginal orientation in group II, e.g., biotite. (2) Concentration of less usual minerals, e.g., andalusite, schorlite, in thickened zones of I, with uniform distribution of tourmaline in II.

WINCHESTER AREA

SKETCH OF THE REGIONAL GEOLOGY

Winchester is situated on the southern edge of the Perris plain. Monadnock-like hills, composed of metamorphic rocks, assigned by Dudley[14] to the Triassic, rise above the plain. These have been invaded by batholithic rocks varying in composition from gabbro through quartz monzonite, emplaced in order of increasing silicity. The geology of the region is discussed by Dudley.[15] In the hill in which the pegmatite in question occurs, schistose rocks are cut by gabbro, each the probable equivalent of a similar rock in adjacent hills. Deep weathering of the metamorphic series handicaps observations, but granitic gneisses and chlorite schists are present in the series.

GEOLOGICAL RELATIONS OF THE PEGMATITES

The andalusite-bearing pegmatite outcrops across the brow of a small hill, in T. 5 S., R. 2 N., Sec. 12 (Elsinore quadrangle). Prospectors have cross-cut the dike at two places, and a shaft descends about 20 feet down the dip. Deep weathering obscures the mineral relations. The dike, which strikes N. 45° W., dipping SW. at 30°, is parallel to the foliation of the metamorphic series and is from six to seven feet thick, with a few small subparallel branches. The dike is lenticular along the strike, pinching irregularly, and dying out completely in about thirty feet. Down the dip, the dike shows no evidence of thinning as far as it is exposed. The second generation pegmatites are represented by a single dike six to eight feet thick, striking N. 10° E. and dipping SW. at 38°. This dike cuts the gabbro, which in turn intrudes the metamorphic rocks. The mineral composition of this second pegmatite is simple, except for beryl and small blue tourmaline crystals.

[14] Dudley, Paul H., Geology of a portion of the Perris block, southern California: *Calif. Jour. Mines and Geol.*, State Mineralogist's Report, **31**, 487–506 (1935).

[15] *Ibid.*

Andalusite

The andalusite occurs in a lens two feet thick along the hanging wall of a simple biotite-quartz-microcline pegmatite. The andalusite lens pinches out down dip within twenty feet. Within the lens andalusite occurs in prism bundles up to three inches long, in pods of partially chloritized biotite. These pods possess no positive orientation in the marginal lens, but the biotite of the pods forms a distinct coating about the andalusite. Such biotite "coronas" are commonly $\frac{1}{4}$ inch thick, with an onion-skin wrapping of biotite plates.

The biotite pods are, in turn, arranged in lenticular groups within the larger lens. The axes of the smaller lenses usually lie across the trend of the larger one. Three or four pods compose these smaller lenses, each in turn enclosing andalusite prism bundles (Fig. 3).

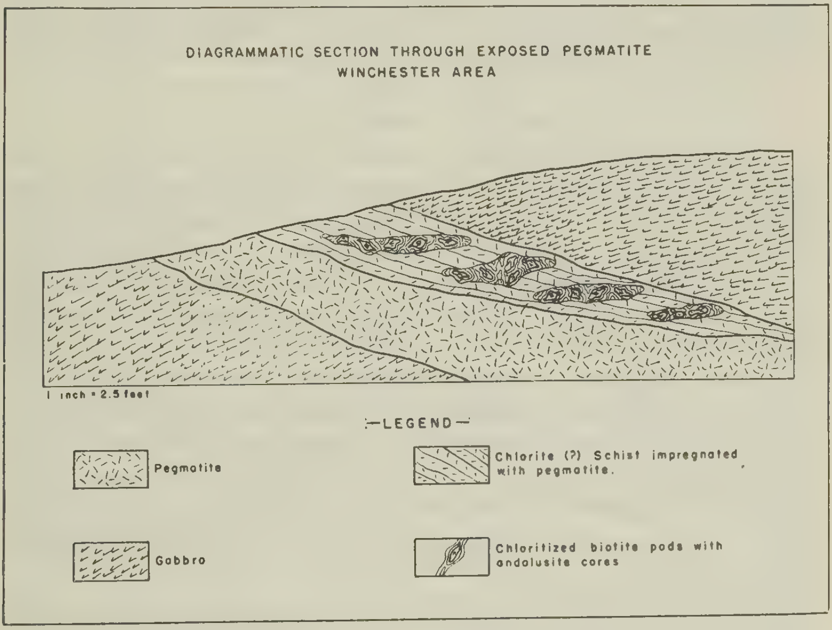
DIAGRAMMATIC SECTION THROUGH EXPOSED PEGMATITE
WINCHESTER AREA
1 inch = 2.5 feet
—LEGEND—
Pegmatite
Chlorite (?) Schist impregnated with pegmatite.
Gabbro
Chloritized biotite pods with andalusite cores

Fig. 3

Corundum

Corundum occurs disseminated in the andalusite prisms, and in euhedral crystals up to three inches in length. The corundum shows color zoning from sapphire-blue to gray. Though intimately associated with the andalusite, the corundum is rarely in parallel orientation with it. The corundum is confined to the andalusite-bearing areas of the dike.

ORIGIN OF ANDALUSITE AND OTHER ALUMINUM SILICATES

INTRODUCTION

The published accounts of andalusite suggest its origin by three general processes: (1) alteration of xenoliths; (2) magmatic sources; (3) concentration from wall rocks under high temperature, accompanied by igneous emanations; or a combination of these processes. The important andalusite deposits in the White Mountains of California have been attributed to metamorphism of aluminous layers by igneous intrusions,[16] as have the deposits of dumortierite and andalusite at Oreana, Nevada.[17] Xenolithic alteration has been suggested for the origin of several deposits of aluminum silicate minerals, notably some of the important kyanite and sillimanite deposits of India.[18] Magmatic emanations have been invoked to explain some small deposits of andalusite,[19] and larger ones of kyanite.[20] Pyrogenic andalusite has also been described.[21]

GENESIS IN THE COAHUILA MOUNTAIN DEPOSIT

Granitic gneisses and biotite-rich schists are typical rocks of the metamorphic sequence in which the andalusite pegmatite is developed. Rarer types are corundum-muscovite and corundum-biotite schists, not present in the immediate area, but found abundantly on the north flank of the San Jacinto Mountains at a locality reported by Hazen.[22] These types are widely distributed in the metamorphic terrain.[23] The metamorphic sequence in Coahuila Mountain is probably equivalent to that of the San Jacinto Range, since xenoliths and pendants of similar type are more or less continuous northwesterly to the known corundum-bearing areas. The original sedimentary character of the metamorphic series is attested by interbedded lenses of marble with relict stratification. Thermal metamorphism is suggested by the presence of abundant graphite in the marble, which is composed largely of grains of calcite one-quarter inch across. Orientation of the flake graphite along relict stratification planes, suggests that the graphite originated from organic matter contained in the limestone. The development of graphite under these conditions has generally been considered diagnostic of high temperatures.[24] Abundant lenticular silexite masses (dikes and veins) are found in the metamorphic terrain. According to Tyrrell,[25] andalusite may form from the alteration of a muscovite-rich rock under thermal metamorphism, when silica is present, by the equation:

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[16] Kerr, Paul F., *op. cit.*, p. 642.

[17] Kerr, P. F., and Jenney, Philip, Dumortierite-andalusite mineralization, Oreana, Nevada: *Econ. Geol.*, **30**, 287–300 (1935).

[18] Dunn, J. A., Andalusite in California and kyanite in North Carolina: *Econ. Geol.*, **28**, 695 (1933).

[19] Macdonald, G. A., and Merriam, R., *op. cit.*, p. 594.

[20] Stuckey, Jasper L., Kyanite deposits of North Carolina: *Econ. Geol.*, **27**, 670 (1932).

[21] Hills, E. S., *op. cit.*, p. 300.

[22] Hazen, Guy E., Corundum crystals—California: *The Mineralogist*, **9**, 81–82, (1941).

[23] Murdoch, J., and Webb, R. W., Notes on some minerals from southern California. III. Corundum and associated minerals near Banning, San Jacinto Mountains, California: *Am. Mineral.*, **27**, 328–329 (1942).

$$H_2KAl_3(SiO_4)_3+SiO_2\rightarrow Al_2SiO_5+KAlSi_3O_8+H_2O$$

That this may have been the course of development of the Coahuila andalusite is suggested by the presence of at least two of the necessary factors for Tyrrell's hypothesis, although original quartz in the muscovite-rich rock may have been the source of silica in the reaction.

Additional evidence in support of generation in place may be deduced from suggestions regarding the origin of the corundum in the dike. The corundum grains, occurring as anhedrons in nests of muscovite, may be interpreted as residual grains from an original corundum-rich rock, the muscovite now enveloping the corundum because it developed by alteration of the corundum itself. Thus an original highly aluminous sediment, subjected to thermal metamorphism developing a muscovite-corundum schist, might by addition of silica, and continued thermal conditions, produce an andalusite-quartz-corundum rock. If reaction between these minerals were incomplete, corundum residuals in andalusite should be expected, especially since muscovite might be looked upon as forming "coronas" about corundum, thus isolating the corundum from further reaction as later chemical changes occurred.

Associated pneumatolytic processes during and following the andalusite formation are evidenced by intergrowth of schorl-tourmaline with andalusite, indicating the introduction of boron. Under these circumstances tourmaline might form by reaction of boron compounds with corundum and quartz.

Corundum, when associated with andalusite, has commonly been considered a late-forming constituent in most pegmatitic occurrences. In attempting to ascertain whether corundum formed before or after the andalusite, it was suggested,[26] since tourmaline formed simultaneously and following the andalusite in this dike, that the presence of boron in the corundum would suggest corundum formation before tourmaline, and therefore before andalusite. Accordingly a spectrographic analysis of carefully sorted corundum granules was obtained, with the following results:

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[24] Clarke, F. W., Data of Geochemistry: *U. S. Geol. Surv., Bull.* **770,** 330 (1924).

[25] Tyrrell, G. W., *Principles of Petrology,* 294 (1926).

[26] Personal communication from Professor G. E. Goodspeed of the University of Washington.

Elements	*Estimated Quantity*	
Al	Principal Constituent	
Si	.1–1%	from andalusite
Fe	.1%	
Ti	.1%	
B	.01%	from tourmaline
Mg	.01%	
Ca	.001%	
Cu	.0001–.001%	

Analysis by Applied Research Laboratories, Glendale, California. Quantities estimated to the closest power of ten.

The analysis is not considered conclusive, but the question may be raised as to where the boron in the corundum originated, unless it were introduced into the corundum when the tourmaline formed. The presence of boron in the corundum may be suggestive of the genetic sequence (1) corundum, (2) andalusite, (3) tourmaline.

Late hydrothermal activity is shown by the sericitic rims about all the andalusite crystals.

The general features of (1) lenticularity, (2) unusual mineral association, and (3) limited distribution of pegmatite are less common features of magmatic pegmatites than of other types. The similar composition of the wall rocks of the pegmatite, both against the dike and in the metamorphic body as a whole, indicates no addition of material from the pegmatite into the wall rocks. Magmatic processes thus seem even more remote as the contributing factors in the origin of the Coahuila pegmatite. Again, the hypothesis of xenolithic alteration may be discarded because the pegmatite is part of a large metamorphic mass of similar composition, which is in itself a huge xenolith, and should on the xenolithic hypothesis be itself partially transformed. The presence of the characteristics just enumerated in themselves suggest generation of andalusite in place by metamorphic differentiation.

GENESIS IN THE WINCHESTER DEPOSIT

Chlorite schists compose the small areas of metasediments included in gabbro intrusives, cut by simple pegmatites, in the Winchester occurrence. The fact that the andalusite is confined to the margin of a single dike, in a large lentil containing pods which simulate xenolithic blebs, separated by biotite-rich gneissic zones, suggests the applicability of the xenolithic hypothesis for the Winchester occurrence. An original argillaceous xenolith under high temperature can be expected to proceed toward the production of andalusite, with simultaneous development of corundum (if the alumina content is high in the inclusion). The rims of chloritic biotite enclosing andalusite prisms may have resulted from the recrystallization of the chlorite of the xenolith since andalusite contains insufficient iron (and no magnesium) to satisfy the biotite forming thereon.

Summary of Genesis

Two andalusite pegmatites are ascribed to the thermal metamorphism of original aluminous sediments; one by thermal metamorphic differentiation in a series of metasediments, producing a pegmatite lens in highly metamorphosed rocks; the other by hydrothermal metamorphism of regionally metamorphosed sediments, included as xenoliths in a simple pegmatite.

Acknowledgments

These investigations have been conducted as part of a program of study of the pegmatites of southern California, in progress with Dr. Joseph Murdoch of the University of California, Los Angeles. His cooperation in reading the manuscript, and in the field, is appreciated. Drs. James Gilluly, Cordell Durrell, and Adolf Pabst kindly criticized the manuscript. The Coahuila pegmatite is owned by Mr. Roy Fairchild of Los Angeles and Mr. Don Roland of Hemet, California, who permitted the writer free access to the deposit. Mr. B. Gordon Funk, former student of the writer, assisted in the field and first brought the deposit to the writer's attention. The Winchester property is owned by Dr. Donald Skillen, Flintridge, California, who likewise permitted study of the pegmatite. Financial assistance was received from the Board of Research, University of California, Los Angeles. All of these services are gratefully acknowledged.

PHASE RELATIONS IN THE SYSTEM CALCIUM ORTHOSILICATE-ORTHOPHOSPHATE

M. A. Bredig.*

Abstract

Two different crystal structures, isotypic with hexagonal α and orthorhombic β-potassium sulphate, occur in calcium orthosilicate containing small amounts of various additions. This, and the fact that γ-Ca_2SiO_4 is isotypic with β-Na_2BeF_4 whose high-temperature, α, form is also isotypic with α-K_2SO_4, leads to the assumption that calcium orthosilicate, above 1420° C, is isodimorphous with potassium sulphate. It is shown how these relations influence the shape of a schematic equilibrium diagram of the system Ca_2SiO_4-$Ca_3(PO_4)_2$.

Many substances containing two or more components have simply been designated as binary, ternary, quaternary, or the like, compounds, no matter how complex molecular formulas had to be ascribed to them, if only they had been observed as individual solid phases, not known in any of the constituent one-component, binary, ternary, and so forth, systems. It has recently been shown by the writer (1, 2) that a number of such allegedly binary, ternary or quaternary compounds actually can be recognized as simple solid solutions, when the identity of their crystal structure with that of a hitherto unknown modification, usually the high-temperature form, of one of their components, is established. In this way, it was shown that for instance "$Ca_4Na_6(PO_4)_4CO_3$" (3) is a solid solution of Na_2CO_3 in the high-temperature form of $CaNaPO_4$, that glaserite "$K_3Na(SO_4)_2$" actually is just a member of the uninterrupted solid solution series $(K,Na)_2SO_4$, between α-K_2SO_4 and α-Na_2SO_4, and that the "compound $Na_8CaS_5O_{20}$" (4) is nothing but a solid solution of $CaSO_4$ in the high-temperature modification of Na_2SO_4 (I).

In the system CaO–SiO_2 -P_2O_5 at least three crystal phases thus far have been obtained, none of which has been known in the binary systems CaO-SiO_2 or CaO–P_2O_5, not to speak of SiO_2–P_2O_5. These are: "$5CaO \cdot P_2O_5 \cdot SiO_2$" (silicocarnotite) (5, 6), "$4CaO \cdot P_2O_5 \cdot SiO_2$" (compound "X" (5) or "B" (7)), and "$7CaO \cdot P_2O_5 \cdot 2SiO_2$" (6, 8). They all were described as ternary compounds of the system CaO–P_2O_5–SiO_2, until the substance "$7CaO \cdot P_2O_5 \cdot 2SiO_2$" was shown by the writer (1, 2) to possess the simple crystal lattice of a group of simple compounds of the type A_2XO_4, such as Na_2SO_4, K_2SO_4, $CaNaPO_4$, $CaKPO_4$, the high-temperature, α, modifications of which form solid solutions with other compounds to an extensive degree. It was therefore concluded that the substance "$7CaO \cdot P_2O_5 \cdot 2SiO_2$" very likely is not a ternary compound but a solid solution of $Ca_3(PO_4)_2$ in Ca_2SiO_4, and that the individual com-

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TABLE 1. ISODIMORPHISM OF α AND α' CALCIUM ORTHOSILICATE WITH α AND β POTASSIUM SULPHATE

Brutto Formula	Designation		Lattice Constants			
	proposed	previous	a_0	c_0	c/a	z^+
α-K_2SO_4	α, hexagonal high-temp. form		5.71^{++}	7.85^{++}	1.37^{++}	2
$Ca_{1.75}Si_{0.5}P_{0.5}O_4$	solid sol. of $Ca_3(PO_4)_2$ in hexagonal α-Ca_2SiO_4	ternary compound "$7CaO \cdot P_2O_5 2SiO_2$" nagelschmidtite ref. (6), (8), (15)	5.38	7.10	1.32	2
Ca_2SiO_4, $.135Na_2O$, $.068\ Fe_2O_3$	solid sol. in hexagonal α-Ca_2SiO_4	—	5.40 (*cf.* footnote 2)	6.996	1.296	2
β-K_2SO_4	β, orthorhombic low-temp. form		a 5.76	b 10.05	c 7.46	4
Ca_2SiO_4, $.09CaK_2SiO_4$	solid sol. of CaK_2SiO_4 in orthorhombic α'-Ca_2SiO_4	ternary compound "$23\ CaO \cdot K_2O \cdot 12SiO_2$" ref. (10)	5.18	9.52	6.77	4
$Ca_{1.93}Si_{.86}P_{.14}O_4$	solid sol. of $Ca_3(PO_4)_2$ in orthorhombic α'-Ca_2SiO_4	"$Ca_3(PO_4)_2 \cdot 12Ca_2SiO_4$" ref. (9)	not reported			4

$^+$ Number of molecules A_2XO_4 per unit cell.
$^{++}$ Measured at 800° C.

pound calcium orthosilicate itself possesses the simple hexagonal crystal structure of the high-temperature, α, forms of the alkali metal sulphates, in some temperature range above its upper transition point at 1420°C.[1]

This view was further strengthened, when a second, well known crystal structure of the type A_2XO_4, that of β-potassium sulphate, was found in yet another ternary combination of a highly complex composition such as $Ca_{27}(SiO_4)_{12}(PO_4)_2$ (9), and also in a substance of the composition $Ca_{23}K_2(SiO_4)_{12}$, which originally had been considered as ternary compound (10). On account of their simple, A_2XO_4 type, crystal structure (TABLE 1), both these substances are now considered as solid solutions, of $Ca_3(PO_4)_2$ and of CaK_2SiO_4, respectively, in a large excess of calcium orthosilicate. Pure calcium orthosilicate also is assumed to possess this structure (henceforth designated α'–Ca_2SiO_4), in addition to the forms α (hexagonal), β, and γ (olivine type). Most probably, α′ is stable immediately above the transition point at 1420°C. Accordingly, the hexagonal, α, structure, isotypic with α-potassium sulphate will have to be assigned to the range immediately below the melting point with a new transition point to be sought in the wide range between 1420° and 2200°C.

The crystal lattice dimensions of both the presumed highest-temperature modifications of calcium orthosilicate, α and α′, are believed to be similar to those given for the solid solutions $Ca_{1.75}(PO_4)_{.5}(SiO_4)_{.5}$ (= "$Ca_7(PO_4)_2(SiO_4)_2$") and $Ca_{1.917}K_{.167}SiO_4$ (= "$Ca_{23}K_2(SiO_4)_{12}$"), respectively, in Table 1, in which the isotypy with α and β potassium sulphate is demonstrated.

Spacings, calculated from the constants given for "$Ca_{23}K_2(SiO_4)_{12}$" in Table 1, are compared in Table 2 with those measured by H. F. McMurdie, as reported by W. C. Taylor (10). The agreement may be considered satisfactory.

In another x-ray diagram of a mixture of "$Ca_{23}K_2(SiO_4)_{12}$" with NaCl, only the lines of the former were diffuse and also the relative intensities somewhat different from those reported by W. C. Taylor. Both facts are regarded as additional evidence that the crystals do not represent a ternary compound, but a solid solution which, in quenching, has suffered a transformation in the solid state from the hexagonal, α, structure to the orthorhombic, α′, structure. The complex polysynthetic twinning demonstrated by W. C. Taylor is considered as a further indication of this solid-phase transformation.

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[1] The author is indebted to Dr. Kenneth T. Greene, Research Associate, Portland Cement Association Fellowship at the National Bureau of Standards for the personal communication that the x-ray data of a solid solution of small amounts of Na_2O and Fe_2O_3 (or Al_2O_3) in calcium orthosilicate also showed the existence of the hexagonal lattice with $a_0 = 5.40$ and $c_0 = 6.996$ Å, $c/a = 1.296$.

TABLE 2. X-RAY PATTERN OF α' CALCIUM ORTHOSILICATE SOLID SOLUTION, $(Ca_{1.917}K_{.166}SiO_4)$
$a_0=5.18$Å, $b_0=9.52$Å, $c_0=6.77$Å, $a{:}b{:}c=0.545{:}1{:}0.700$.

hkl orthorhombic	d_{hkl} calc.	$d_{hkl}(10)$ exp.	Intensity (10)
022	2.765	2.75	v.s.br.
130	2.71		
$Ca(OH)_2$?	2.63?	2.63	w.
220	2.28	2.29	w.
041	2.24	2.24	w.
013	2.195	2.185	m.
113	2.025	2.034	m.
042	1.950	1.959	s.
	etc.		

The specific gravity, calculated from the lattice constants with the assumption of $Ca_{23}K_2(SiO_4)_{12}$ actually representing the mass content of 6 unit cells, is 3.43, which compares with 3.24 as measured experimentally.[2] The disagreement very likely results from the fact that in the calculation more than 4, namely 4.17, cations, Ca and K, were placed in the unit cell beside $2SiO_4$. If the mass content is reduced in the ratio 4:4.17, the specific gravity becomes 3.29 which is in better agreement with the experimental figure 3.24. It would however mean that 4% of the SiO_4 positions were unoccupied. Further efforts are therefore required to clarify this point.

The lattice constants, given by R. Klement and R. Uffelmann (11), of the hexagonal high-temperature modifications of $CaNaPO_4$, $CaKPO_4$ and of other analogous substances of the type A_2XO_4 with which α-potassium sulphate (1, 2) and α-calcium orthosilicate were shown to be isotypic, have as little physical reality as those of the low-temperature, β, form of $CaNaPO_4$ (isomorphous with β–K_2SO_4 and α'–Ca_2SiO_4), as calculated by Klement and Dihn (12), which were shown to be erroneous (2). The interpretation by M. A. Bredig of the x-ray patterns of the high-temperature forms of these substances is supported by the results, independently obtained by L. S. Ramsdell (13) on α–Na_2SO_4 ($a_0=5.38$, $c_0=7.26$ Å, $c/a=1.35$), and by O'Daniel and Tscheischwili (14) on $\alpha=Na_2BeF_4$ ($a_0=5.31$, $c_0=7.08$ Å, $c/a=1.335$).

In the results of the latter authors additional confirmation is found in support of the assumption that in regard to crystal structure at high temperatures calcium orthosilicate is analogous to the alkali metal sulphates. Na_2BeF_4 was shown by them to be isotypic with γ–Ca_2SiO_4. In Table 2, Na_2BeF_4 is demonstrated to be also isotypic, at elevated temperatures, below its melting point, with the solid solution of calcium phosphate in calcium orthosilicate, $Ca_{1.75}(PO_4)_{.5}(SiO_4)_{.5}$.

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[2] Personal communication from Dr. W. C. Taylor, Portland Cement Association Fellowship, National Bureau of Standards, Washington, D. C.

TABLE 3. ISOTYPY OF α- AND β-Na_2BeF_4 WITH α- AND γ-Ca_2SiO_4

Brutto Formula	Designation	z*	a_0 Å	b_0 Å	c_0 Å	$a:b:c$
			1. Low-Temperature Forms (orthorhombic):			
Na_2BeF_4	β	4	4.892	10.90	6.560	0.4488:1:0.6019
Ca_2SiO_4	γ	4	5.06	11.28	6.78	0.4485:1:0.6011
			2. High-Temperature Forms (hexagonal):			
Na_2BeF_4	α	2	5.31	—	7.08	$c/a=1.335$
$Ca_{1.75}Si_{.5}P_{.5}O_4$	α (solid solution)	2	5.38	—	7.10	$c/a=1.320$

* z = number of molecules of Brutto formula per unit cell.

O'Daniel and Tscheischwili consider the isotypy of Ca_2SiO_4 and Na_2BeF_4 as limited to the low-temperature modifications, the isotypy of α–Na_2BeF_4 and $Ca_{1.75}Si_{.5}P_{.5}O_4$ apparently not being known to them. They mention the lower symmetry of the high-temperature, α- and β-phases of calcium orthosilicate which, accordingly, could not be considered by them isotypic with the hexagonal high-temperature form of Na_2BeF_4 (α). However, as mentioned above, the validity of our previous knowledge of α–Ca_2SiO_4 is now very doubtful (1). It has also been shown that, although each of the compounds Na_2SO_4, K_2SO_4, $CaKPO_4$, and others, has its own individual orthorhombic crystal structure at room temperature, they are isotypic in their high-temperature modifications. This is in full agreement with expectation. Not only will substances of the type mentioned show at low temperatures the greater influence of the individual ions, but are also believed to be necessarily isotypic at high temperatures (where the influence of the individuality of the ions was shown to be diminished), if they are already isotypic at room temperature. An example is the isodimorphism of $CaNaPO_4$ and K_2SO_4. It is therefore believed that the isotypy of β–Na_2BeF_4 with γ–Ca_2SiO_4 together with the isotypy of α–Na_2BeF_4 with $Ca_{1.75}Si_{.5}P_{.5}O_4$ represents strong additional evidence for the assumption that α–Ca_2SiO_4 is isotypic with hexagonal α–Na_2SO_4, α–K_2SO_4, α–$CaNaPO_4$, α–Na_2BeF_4, and the other members of this group of compounds of the type A_2BX_4. Further attention may be given to the fact that the transformation of the low-temperature, γ-form of calcium orthosilicate into the hexagonal highest-temperature α-modification is preceded by the transformation into the middle-temperature form β and, in addition, probably into the other form α', isotypic with β–K_2SO_4, while the low-temperature form of $Na_2BeF_4(\beta)$ transforms directly into the hexagonal high-temperature modification (α). This must naturally be connected with the much higher melting point, that is the much wider temperature range of stability of solid calcium orthosilicate, which is due to the higher electric charge of the ions involved.

Observations on the system CaO–P_2O_5–SiO_2 were summarized by Barrett and McCaughey (15) in two equilibrium diagrams. Together with the considerations of the preceding paragraphs, the following points are bound to cause considerable changes in those diagrams:

1. No melting point maxima have been reported for any ternary compounds such as "$5CaO \cdot SiO_2 \cdot P_2O_5$" or "$7CaO \cdot 2SiO_2 \cdot P_2O_5$." Troemel and Koerber (8) who also considered both substances as ternary compounds state only that their melting points must lie somewhere above 1750°C.
2. Klement and Steckenreiter (4) claim to have obtained a high-temperature phase of the composition of "$5CaO \cdot SiO_2 \cdot P_2O_5$," of a crystal structure different from that of silicocarnotite but analogous to that of "$7CaO \cdot 2SiO_2 \cdot P_2O_5$" which was shown now to be that of α–Ca_2SiO_4.

Although the lack of sufficient data at the very high temperatures of the liquidus curves makes considerable caution imperative, an equilibrium diagram of the system Ca_2SiO_4–$Ca_3(PO_4)_2$, which is thought to conform best with the information available at the present is given in the figure. It is obvious that, contrary to previous such diagrams, no intermediary compounds in equilibrium with the liquid melt are assumed here. Silicocarnotite -according to the experimental result of Klement and Steckenreiter -is assumed to transform into the hexagonal phase before melting. Whether this transformation is characterized by a peritectoid or a dystectoid temperature maximum of the stability of the silicocarnotite phase, cannot actually be stated. Also, the areas of the hexagonal highest-temperature, α, phase of calcium orthosilicate and of the second high-temperature, α', phase were terminated in this diagram by eutectoids at relatively high temperatures, although these phases actually were observed at room temperature. It is considered likely that at low temperatures these solid solutions are metastable only.

The following recent publications became known to the writer while the paper was in the press:

G. Troemel (17) proposes a somewhat different diagram for the system calcium orthosilicate-orthophosphate. His phase "K" (so designated for its isotypy with β-K_2SO_4) is identical with the phase α', while his phase

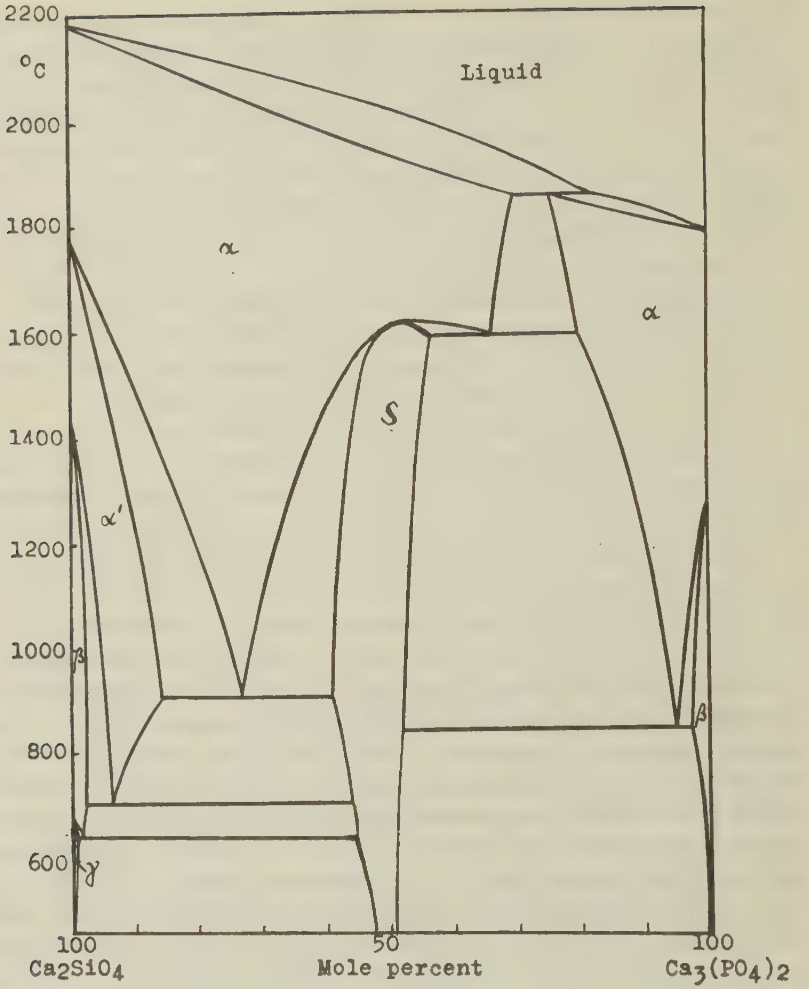

Fig. 1. Schematic Equilibrium Diagram of the System Ca_2SiO_4–$Ca_3(PO_4)_2$.

"R" (for rhenanite, refs. 1 and 3) is identical with hexagonal, α, calcium orthosilicate. Troemel's suggestion to consider "K" and "R" as intermediary phases between those of calcium orthosilicate and orthophosphate, if not as intermediary "compounds," must be rejected on the grounds discussed in the present paper.

H. O'Daniel and L. Tscheischwili (18) found both strontium and barium orthosilicates to be isotypic with β potassium sulphate. In connection with the observation, by N. A. Toropov and P. F. Konovalov

(19), of solid solutions of calcium and barium orthosilicates, this may be considered another indication for the occurrence of the β potassium sulphate structure in the individual compound calcium orthosilicate (α').

S. Zerfoss and H. M. Davis (20) investigated the influence, not of $Ca_3(PO_4)_2$, but of P_2O_5, on the transitions in calcium orthosilicate. Their low value for the solid solubility of P_2O_5 therefore must not be considered to be in disagreement with the relations postulated in the present paper.

ACKNOWLEDGMENT

The cooperation of Dr. W. C. Taylor, Research Associate, Portland Cement Association Fellowship at the National Bureau of Standards, Washington, D. C., and of Professor Lars Thomassen of the University of Michigan, Ann Arbor, Mich., in supplying a sample of $Ca_{23}K_2(SiO_4)_{12}$, and in preparing an x-ray picture thereof, respectively, is gratefully acknowledged.

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NOTES AND NEWS

AN UNIDENTIFIED MINERAL IN THE QUARTZ BASALT OF LASSEN VOLCANIC NATIONAL PARK, CALIFORNIA

Richard Merriam and T. G. Kennard.*

The occurrence of an unidentified mineral at Cinder Cone, Lassen Volcanic National Park, California, was pointed out to the senior author by Dr. W. I. Gardner. The former subsequently visited the locality and with the aid of Mr. Rondo Birch collected sufficient material for optical determinations and spectrographic analyses.

Occurrence

The geology of Cinder Cone has been well described by Finch and Anderson,[1] as well as by Williams.[2] They state that the volcanic history began with pyroclastic eruptions which built up a cone. A lava flow from the base of the cone was followed by another series of pyroclastic eruptions. Following a period of quiescence there were four or five eruptions of lava from the base of the cone, the last probably occurring about 1851. Small cinder cones indicate the presence of vents under the lava field. Opaline deposits locally cementing the pyroclastic material are accounted for as the work of steam vents.

Petrography

The cone and flows are composed entirely of quartz basalt. The lava is dense black or gray in color, mostly vesicular, but rarely massive. In places it exhibits "aa" or "pahoehoe" surfaces but the greatest part is of blocky character. The texture is microporphyritic with phenocrysts of plagioclase, olivine, and enstatite. Labradorite and augite microlites and pale-brown glass make up the groundmass. Quartz xenocrysts averaging 1–2 mm. in diameter are surrounded by coronas of diopsidic augite and glass. Inclusions range up to 15 cm. in length and are dacitic (quartz-oligoclase-sanidine-glass), with sanidine and quartz. It was suggested[1,2] that these inclusions were derived from a differentiated dacite magma, the quartz basalt thus being a hybrid rock.

Old fracture surfaces have a varnished appearance similar to that of desert varnish, areas adjacent to quartz xenocrysts being especially glassy. Microscopic examination reveals that the appearance is due to incipient fusion of minerals at the surface. Local oxidation has intensified the red color of the ferromagnesian minerals.

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[1] Finch, R. H., and Anderson, C. A., The quartz basalt eruptions of Cinder Cone, Lassen Volcanic National Park, California: *Univ. Calif. Publ., Bull. Dept. Geol. Sci.*, **19**, 245–273 (1930).

[2] Williams, Howel, Geology of Lassen Volcanic National Park, California: *Univ. Calif. Publ., Bull. Dept. Geol. Sci.*, **21**, 195–385 (1932).

Glass exposed on the old fractured surfaces is commonly light-blue in color. Crusts of a bluish-green mineral have crystallized on many of these surfaces. Such areas appear as small (1–2 mm.), shiny, blue-green spots and consist of aggregates of plates and fibers lying more or less parallel to the surface. Crystallization has also occurred in cracks penetrating the glass and, in some instances, crystals appear to have developed entirely within the unfractured glass. The blue-green mineral is commonly associated with the blue glass but does occur with the colorless type.

Optical and Other Properties of Glass and Blue-Green Mineral

Optical and crystallographic properties were determined as far as possible on the material at hand and with the equipment available. Thin sections and immersion oils were used. The refractive index of the glass varies from 1.500 to 1.525. Apparently there is no relation between this property and color.

The blue-green mineral appears to be triclinic (nearly monoclinic with $Y=b$). Good cleavages are exhibited on planes that were taken to be (001), (100), and (010). The angle $001 \wedge 100$ is probably $68° \pm 5°$. Most grains, although crystalline, are irregular, roughly tabular or prismatic. Fibrous or platy aggregates are common. Indices of refraction determined in oils are: $\alpha=1.545$, $\beta=1.565$, $\gamma=1.575$; $\gamma-\alpha=.030$, all $\pm.002$. The negative 2V, roughly determined from interference figures, $=50°–60°$. Dispersion of the optic axes is $r>v$, strong. The optic axial plane is nearly normal to (010). In sections normal to Y the angle $Z \wedge c$ is 14° and the apparent angle $001 \wedge 100$ is 66°. Cleavage flakes lying on (010) usually show $Z \wedge c=18°$ and $001 \wedge 100$ is approximately 71°. No pleochroism is perceptible, the color being uniformly blue-green.

The specific gravity determined in bromoform is $2.60 \pm .02$. The hardness is approximately 3.

Chemical Composition

As yet sufficient material has not been concentrated for quantitative chemical analyses. However, the results of spectrographic examinations by Kennard (Table 1) show the qualitative, and approximate quantitative composition. It is probable that the iron and copper shown in group two are responsible for the color of the mineral and glass, and are essential to the formula of the mineral. The weight percentage of copper is probably between 1 and 5%, though possibly it exceeds 5%.

TABLE 1. SPECTROGRAPHIC ANALYSIS OF BLUE GLASS AND BLUE-GREEN MINERAL FROM CINDER CONE

T. G. KENNARD, *analyst*

	BLUE GLASS	BLUE-GREEN MINERAL
Large amount	Al	Al
	Si	Si
Small amount: X%	Ca	Ca
	Mg	Mg
	Fe	Fe
	Cu	Cu
Very small amount: 0.X%; possibly 0.0X%	Li	Li
	Na	Na
Traces: 0.0X to 0.00X%	B	B
	Ba	Ba
	Mn	Mn
	Pb	Pb
	Ti	Ti

FACTORS INFLUENCING THE DISTRIBUTION OF THE ELEMENTS

James H. Pannell, *Niagara Falls, New York.*

The relative abundance of the elements in the earth's crust is a subject of fundamental importance to mining geologists but is one which is seldom studied comprehensively. A great number of the elements present in the earth in very low concentration are being used in every day artifacts, and it has become essential to discover the factors causing these metals to become concentrated in certain rocks. The search for many of the rarer metals has been stimulated by their increasing use in the realms of catalysis and electron emission ,where the quantity used is quite small.

At this time, when the search for strategic materials is the basis of production, it would seem advisable to review briefly our knowledge concerning the causes for the present distribution of minerals. Although such knowledge will not lead us immediately to a source of rich ore, it will save us the time which might be spent in prospecting for material in an impossible location.

This study received a great and much-needed impetus between the years 1910 and 1920, due mainly to the work of F. W. Clarke in the U. S. and V. M. Goldschmidt in Germany. The latter, by his use of visual and *x*-ray spectrography, successfully covered a great deal of ground and eliminated the error introduced in chemical analysis by the impurities in the large quantities of reagents necessary for the treatment of large samples. His determinations of ionic radii, carried out as a part of this work, will stand as a lasting memorial to his perseverance.

The average percentage composition of the earth's crust is now known to a high degree of precision, and the following table is taken principally from the results obtained by Clarke and Washington (1). It is worth remembering that although these figures relate to the lithosphere only, the inclusion of the atmosphere and hydrosphere does not alter them, as they stand.

Many of the elements in this table, for instance radium, beryllium, molybdenum, vanadium and tungsten, which are exceedingly scarce, have become quite familiar to us as a result of their highly important chemical and physical properties. Their use, however, would be prohibited if they had not been concentrated by natural processes in certain parts of the earth's crust to such an extent that their extraction is relatively simple.

In 1922 V. M. Goldschmidt (2) suggested that the scarcity of the precious metals was not an inherent characteristic of planetary bodies, but was caused by a process of selective elimination, because of the large partition ratios of these elements between silicate slags and ferro-compounds.

THE CHIEF ELEMENTS OF THE EARTH'S CRUST
IN ORDER OF ABUNDANCE

1. Oxygen	46.43	23. Lithium	0.003
2. Silicon	27.77	24. Copper	0.002
3. Aluminum	8.14	25. Cerium etc.	0.001
4. Iron	5.12	26. Beryllium	0.00xx
5. Calcium	3.63	27. Cobalt	0.00xx
6. Sodium	2.85	28. Boron	0.000xx
7. Potassium	2.60	29. Zinc	0.000xx
8. Magnesium	2.09	30. Lead	0.000xx
9. Titanium	0.629	31. Arsenic	0.000xx
10. Phosphorus	0.130	32. Cadmium	0.0000xx
11. Hydrogen	0.127	33. Tin	0.0000xx
12. Manganese	0.096	34. Mercury	0.0000xx
13. Fluorine	0.077	35. Antimony	0.0000xx
14. Chlorine	0.055	36. Molybdenum	0.0000xx
15. Sulphur	0.052	37. Silver	0.00000xx
16. Barium	0.048	38. Tungsten	0.00000xx
17. Chromium	0.037	39. Bismuth	0.00000xx
18. Zirconium	0.028	40. Selenium	0.000000xx
19. Carbon	0.027	41. Gold	0.000000xx
20. Vanadium	0.021	42. Bromine	0.000000xx
21. Nickel	0.019	43. Tellurium	0.0000000xx
22. Strontium	0.018	44. Platinum	0.0000000xx

A comparison of the lithosphere with iron meteorites reveals a striking richness of the latter with respect to the rarer metals, germanium and gold. Most geologists favor the theory which proposes that the core of the earth consists of an iron-nickel combination similar to that which constitutes the magnetic portion of iron meteorites, although recently a novel hypothesis of an "electronic gas" (3) has been propounded for the earth's centre and its implications may have some effect on this part of our argument. The process of equilibrium between iron and large quantities of silicates was verified by experiments with artificial melts and by a study of the natural iron concretions in the Ovifak basalt on the island of Disco near Greenland. The enrichment of these is illustrated by the following figures, giving amounts in grams per ton: Pt 5, Pd 1, Rh 0.5, Ru 0.5, Au 1–5, Ag 5–10, Ge 1000. Although H. S. Washington (4) discovered an interesting relationship between the periodic classification and the correlation of the elements, this was probably mere happenstance because there is no similar line of demarcation in the long periodic table.

A classification based on the distribution of the elements has been made by Goldschmidt (2) in which he divides them into five groups. The Siderophile, Chalcophile and Lithophile correspond to the Iron, Sulphide and Silicate respectively; the inclusion of the Atmophile and

Biophile would make the range complete, but they are not pertinent to this sketch. The Siderophile includes the transitional metals, iron, nickel, cobalt, etc., and the noble metals. In the Chalcophile are the heavy metals and metalloids, while the Lithophile contains the alkali metals, alkaline earths, halogens and the lighter metals. When considering natural processes of differentiation we must not expect to find any truly perfect separations and thus some elements occur in all classes. According to this plan then, the three concentric spheres of which the world consists are iron-nickel at the centre, sulphide intermediate, and silicate at the surface, with one of the boundaries coinciding with the limiting depth for the propagation of transverse vibrations, and beyond which the texture of the bathysphere must alter considerably. There have been many schemes suggested for the general composition of the earth and these are reviewed by A. F. Buddington (5) who does not belive that the idea of such a large volume of sulphide is tenable. He gives the siderophile a mean thickness of twenty kilometres, and places it at a distance of twenty-nine hundred kilometres from the surface. Nevertheless, the main idea of magmatic differentiation is generally conceded to have been the first step in separating the elements.

During magmatic crystallization, when the space lattices of minerals are being built up of ions or atoms, another course of selection takes place. The growth of a crystal in a saturated solution of the salt can be visualized as an orderly falling into place of alternate positive and negative ions so that each small unit cell is electrically neutral. If one now introduces another cation similar to that already present, but having a smaller ionic radius, it will take the place of the larger ion in the subsequent crystallization. Similarly, in mineralization the smaller ion has a greater chance of going into the crystal, as it permits a tightening up and decrease of lattice energy. In silicates however, when an isomorphous replacement of silicon by aluminum takes place, an alkali metal is also added and this cation merely fits into an interstice and is not close-packed. Base exchange is not a new concept by any means and its importance in agriculture (6) must have been appreciated at an early stage. Instances of this action are so common that one may discern, by the determination of the alkali metals in a mixture of plagioclases for instance, which of them crystallized first. The ionic radii of these cations are: Li 0.78; Na 0.98; K 1.33; Rb 1.49; Cs 1.65 angstrom units. A great deal of controversy has raged over the preferential movement of these alkalis in ionic exchange as some experimentalists found them to be arranged in reverse order to their radii and hence postulated a "hydrated ion" with an envelope inversely proportional to the effective radius (8). A mathematical expression for this mechanism was worked out by Hans Jenny (8) in a thorough study of the aluminum silicates. Recently Russell and Pearce (7) were able to separate a mixture of the rare earths by percolating their solution through a zeolite and making use of the fact that the smaller ion is extracted first and held out most firmly. An ion of practically the same size but of higher valency than another will also be found in the early crystals of a melt, and an example of this is seen in the preponderance of anorthite-$CaO \cdot Al_2O_3 \cdot 2SiO_2$ in the early fractions of sub-alkaline granodiorites. Similarly, the last crystals of magnesium minerals contain most of the lithium present. The following tables summarize these data, and are from the work of Goldschmidt (2).

Differentiation During Crystallization

Figures relate to the quotient by weight

$1000 \times Li_2O/MgO$

Early Rocks		*Late Rocks*	
Peridotite	0.12	Syenite	20
Gabbro	3.3	Granite	600
Diorite	10	Trachyte	150
Basalt	3.3	Obsidianite	200
Porphyrite	16		

Percentages of Certain Oxides in Rocks

	Peridotite	Gabbro	Diorite	Granite	Nepheline syenite
Early					
Cr_2O_3	0.5	.05	.01	.0003	.0001
NiO	.4	.02	.005	.0003	.0003
CaO	.03	.01	.004	.001	.001
MgO	40.	8.	3.	1.	1.
Late					
BaO	.003	.007	.03	.05	.06
Cb_2O_5	—	.001	.003	.005	.02
La_2O_3	—	.001	.003	.005	.05
K_2O	.1	1.	2.	4.	6.

Early	*Silicate Meteorites*	*Earth's Crust*
Chromium	3,200 grams per ton	200 grams per ton
Magnesium	137,000 grams per ton	21,000 grams per ton
Late		
Zirconium	80 grams per ton	190 grams per ton
Sodium	3,700 grams per ton	21,400 grams per ton
Lithium	5 grams per ton	65 grams per ton
Potassium	1,700 grams per ton	25,900 grams per ton
Strontium	20 grams per ton	420 grams per ton
Barium	5 grams per ton	390 grams per ton

Some idea of the marked effect which a small difference in radii between two cations can have on their separation is gained from the higher gallium: aluminum ratio in later minerals, their respective radii being 0.62 and 0.57 angstrom units.

A comparison of the earth's crust with silicate meteorites shows that the former contains a disproportionately large amount of late crystals in its uppermost layers, and the above table expresses this quantitatively. The effect is mainly due to the low density of the syenites and granites of which the Sial is composed, and is an example of gravity differentiation. Two well-known examples of this are the Lugar Sill, where olivine crystals sank to the lower regions of the magma, and the Murray ore deposits at Sudbury.

Probably the first attempt to correlate the elements was made by Washington (10, 11) but in spite of the number of analyses he made, his knowledge of the chemical compositions of minerals was not comprehensive enough to enable him to arrive at any worthwhile conclusions. At that time the only relationship recognized was that propounded by Vogt (12) which merely indicated which elements were likely to be found in acid or basic rocks. Thus the siliceous rocks will contain higher proportions of aluminum and alkalis, while ferromagnesian minerals will be found in basic rocks, where the term "basic" implies an unsaturated condition with respect to silica. This division is important as a basis for the study of petrology but it is too simple to be used as a guiding rule in an investigation.

Among the many interesting and provocative groups, so far as abundance is concerned, is that containing titanium. This element is ninth in order, according to Clarke, and hence is much more abundant than any of the other members of its class, viz., zirconium, hafnium, and thorium. In fact, the average amount in the earth as a whole is probably less than 0.2% (9); although much of the titanium may crystallize early, it probably associates with zirconium, hafnium and thorium, which are conspicuous members of the later crystals. As the early dense minerals separate out, the residual magma becomes enriched in these elements, and this may account for the statement of Lord Rayleigh, obtained through his study of the thermal equilibrium of the earth, that the proportion of thorium decreases with depth. There are no hafnium minerals, as the concentration in the lithosphere is only about 3.2×10^{-4} and a zirconium: hafnium ratio of about 60:1 prevails. This ratio is not altered by weathering of the minerals, in contrast to the effect on eudialite, in which the $TiO_2:ZrO_2$ ratio may change drastically. Titanium, often in the form of ilmenite ($FeO\cdot TiO_2$), is very widespread but at the same time is so finely divided that at one time it was practically ignored in the analysis of silicate rocks. Another widespread element, strangely enough, is gold and Newton Friend suggests that in the colloidal form it accounts for the color of celestite.

We have seen how important ionic radius and charge is in the distribution of minerals of magmatic origin, and the quotient of these quantities, Z/r plays a vital part in the reactions which lead to the secondary disposition of the elements (2, 13). This ionic potential serves as a key to their behaviour during the metamorphism of rocks. During the processes of weathering, those of low potential, such as the alkali metals, remain in solution as ions; those of intermediate potential are precipitated as hydroxides, and those of high potential form soluble complex anions with oxygen. Chromium and boron are members of the last group. Whether the first continents were formed by radial or tangential forces may be disputable, but since their inception they have been subjected to a continuous leaching action. The mechanical aspect of this affair is known as erosion but it is not of more importance than the effect of solution. A survey of the balance of elements in sea water leads to some surprising revelations, and these are of particular interest now that it is becoming a source for iodine, bromine, and magnesium, to mention only a few. As rich ores are used up and mechanical treatment is progressively improved to handle the poorer ones, it is inevitable that attention will be drawn to the illimitable reserves which the ocean contains. As a result of the work of Joly (14) and others, it is calculated that six hundred grams of igneous rock have passed into solution for every kilogram of sea water, but of the elements with low potential, sodium alone remains to any extent. Some of the others are readily adsorbed on the hydrolysates; beryllium and gallium necessarily are associated with aluminum and occasionally with vanadium also. The concentration of some anions however, is higher than would result from the weathering of primary rocks and their percentage in fossil shells indicates that this concentration was formerly even higher. One is led to believe that they were original constituents and may have been supplied to a large extent by submarine volcanoes. With regard to the poisonous metalloids and heavy metals, it is clear that sufficient amounts have been supplied to drastically alter marine life and consequently terrestrial life too. Fortunately many metals, among which are selenium, arsenic, lead, antimony, and bismuth, are adsorbed by the precipitate of iron hydroxide and subsequently are found in the sedimentary iron ores. Indeed the removal of this arsenic has presented a problem to the steel maker. Copper remains in the sea to a comparatively large extent, in some inexplicable manner and is even found in the shells of oysters (15). However copper is among the rarer elements, in spite of its familiarity in artifacts. Interest is shifting more and more to sea water and bitterns as sources of industrial chemicals and the study of oceanography is certain to increase. An exciting speculation might center about the use of alluvial iron ore beds which are formed when the colloidal hydroxide is coagulated by the ionized salt of the sea. In cases where the gangue is relatively innocuous both iron and aluminum may be extracted, although the latter will undoubtedly be the most valuable.

Metamorphism and more particularly metasomatosis, or changes involving chemical transformation, are responsible for most ore bodies, but, like oceanography, this is a vast subject and will not be dealt with here in any detail. Ignoring for the present the possibility of differentiation, we generally picture the formation of a batholith as an injection of a large mass of molten magma into the overlying rock. Occasionally these intrusions are unbelievably large, e.g., the one in British Columbia, but large or small they are all surrounded by areas of contact metamorphism. Pneumatolysis, resulting from the action of the magmatic vapors, gives rise to ore bodies and the formation of such attractive gems as tourmaline and topaz. The presence of water in this residual liquid from the magmatic crystallization plays an important role in lowering the fusion point of the matrix; one to two per cent can effect a lowering of as much as 300°C. The volatile constituents become concentrated as cooling proceeds and the pressure rises, until finally they are injected with great force into the country rock. Rare elements are so concentrated in the resulting pegmatites that they may crystallize as distinct species, and these minerals in turn are often enriched in extremely rare elements, e.g., rhenium in molybdenite. The action of water vapor and hydrogen chloride, fluoride and sulphide, etc., at elevated temperatures is so little understood that we have no fundamental knowledge by which we may distinguish it from earlier magmatic separations. The chemical activity of these substances under such conditions is very intense and does not easily lend itself to laboratory study. The gases emitted by the fumaroles in the Valley of Ten Thousand Smokes, at temperatures as high as 640°C., were analyzed by Allen and Zies (16) with these results:

99.5% water vapor
0.2% insoluble gases
0.3% acid gases

Although the proportions are quite small, the total volumes of acid gases involved are very large, and in 1919 they totalled 1.8×10^6 metric tons per annum, at normal temperature and pressure. At this location it was found that barium and iron oxides had been concentrated to an amazing degree and at the temperature prevailing, the halides and some-times the sulphides and oxides of the elements encountered were volatile. Although the expulsion of volatile constituents marks the end of igneous activity, it does not terminate the active concentration of elements either by gaseous action or by co-precipitation, which Zies considers to be of great importance. The magnetite found in this valley in 1919 by Fenner was not encountered in 1923, presumably because the temperature had fallen to the point at which condensation of acidic steam took place and decomposed the iron sulphide. In place of this were covellite, chalcocite, and sphalerite which are relatively insoluble in acid and represented a further concentration of copper and zinc.

We would not expect elements which occur in extremely small proportions to be concentrated to an extent that would make their extraction easy, especially when they are so sparsely distributed as to exclude the possibility of forming definite compounds. But, as previously noted, these elements may be trapped or co-precipitated during the formation of other minerals. Among the instances of this are the association of fluorine with barium sulphate and gallium with zinc sulphide. Grimm has also shown how the formation of mixed crystals depends on the dimensions of similar crystals and also on the size of the substituted atomic species. As examples of the combination of rarer elements with common ones having similar characteristics, we may cite aluminum-gallium, magnesium-nickel, zirconium-hafnium, and silicon-germanium. Germanium is also concentrated by certain plants and has been determined to form 1.6% of certain coal ashes. It is interesting to note the association of vanadium, nickel and molybdenum with hydrocarbons, in view of the use of these metals as catalysts in the synthesis of organic compounds. Boron, arsenic, bismuth and beryllium are also present in coal ashes in percentages between 200 and 50 times their percentages in the lithosphere.

Summarizing the three principle factors in the distribution of the elements, they are: the division among the three immiscible spheres of the siderophile, chalcophile and lithophile; separation during crystallization governed by ionic size and charge and the further concentration during the formation of sediments which is controlled largely by the ionic potential. From that point, there are many more factors coming into play which are studies in themselves.

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PAPERS PUBLISHED IN THE BULLETIN OF THE GEOLOGICAL SOCIETY OF AMERICA OF SPECIAL INTEREST TO MINERALOGISTS

The following list of papers of special interest to mineralogists appeared in the January-June numbers of the *Bulletin of the Geological Society of America*. Any of these papers may be secured by writing to the Secretary of the Geological Society of America, 419 West 117th St., New York, N. Y.

Volume 54 (1943)

January–June

Geology and mineralization of the San Antonio mine, Santa Eulalia district, Chihuahua, Mexico. By William Paxton Hewitt, pp. 173–204	$.20
Elasticity of igneous rocks at high temperatures and pressures. By Francis Birch, pp. 263–286	.15
Plagioclase twinning. By R. C. Emmons and R. M. Gates, pp. 287–304	.20
Helium measurement. I. Preliminary magnetite index. By Patrick M. Hurley and Clark Goodman, pp. 305–324	.15
Meteorites and an earth-model. By Reginald A. Daly, pp. 401–456	.30
Origin of sulphides in the nickel deposits of Mount Prospect, Connecticut. By Eugene M. Cameron, pp. 651–686	.30
Phosphatization at Malpelo Island, Colombia. By Duncan McConnell, pp. 707–716	.10
Weathering of igneous rocks near Hong Kong. By W. W. Brock, pp. 717–738	.15

BOOK REVIEWS

MINERALS IN WORLD AFFAIRS. By T. S. LOVERING, Professor of Economic Geology, University of Michigan. Prentice-Hall, Inc. Pp. 394, 40 illustrations, Price $4.00.

The overwhelming importance of minerals in the genesis of war, its conduct and final outcome is rapidly becoming a matter of general knowledge. It is inevitable that the significance of the mineral industries and the consequence of the part that they play in human affairs will receive increased attention from the public in the post-war years. It is also apparent that more educational institutions will be inclined to add course instruction to their curricula covering this field. The publication of Dr. Lovering's, "Minerals in World Affairs" is fortunate in that it presents data which can be read with interest and profit by the non-technical reader and which can serve as a text for organized instruction.

The value of the discussion of present day conditions is enhanced by the inclusion of an historical background of industrial development. The role of minerals in primitive commerce, relationship to national power and military strength, place in national economy and peculiar economic problems is presented. A chapter devoted to the fundamentals of geology and their relationship to mineral deposits supplies the reader with a necessary technical background.

Discussion of mineral commodities is restricted to the basic sinews of war and peace; coal, petroleum, iron and steel, the ferro-alloy elements, and the common nonferrous metals. Completeness of the industrial significance of each commodity is attained by the inclusion of geology, technology, utilization, and international distribution which is illustrated by maps showing world wide dispersion. An appendix containing production tables of representative years supplies factual data. In the past such information could be found only by laborious search through a widely scattered and voluminous literature. The author is to be congratulated on having assembled a comprehensive picture of the role and influence of the common minerals in modern society.

W. M. MYERS

School of Mineral Industries,
The Pennsylvania State College.

AFRICAN HANDBOOKS: 2. THE MINERAL RESOURCES OF AFRICA by A. WILLIAMS POSTEL. The University of Pennsylvania Press, 3622 Locust St., Philadelphia. **1943**, Price $1.50 (paper cover).

This is one of a series of seven "African Handbooks." This pamphlet of 105 pages contains much statistical data on the mineral resources of Africa. The seven chapter headings are: I Base metals (iron, tungsten, manganese, nickel, chromium, molybdenum, cobalt); II Non-ferrous metals (copper, aluminum, tin, lead, zinc); III Minor metals (titanium, beryllium, radium and uranium, antimony, arsenic, cadmium, columbium and tantalum, magnesium, mercury); IV Precious metals (platinum, gold, silver); V Non-metallics (coal, petroleum, diamonds, asbestos, mica, corundum, phosphate, diatomite, fluorspar, graphite, talc, gypsum, sodium compounds, pyrite, barite, slate, building stone, lime and cement); VI Water power and supply; and VII Madagascar. An appendix lists the geographical distribution of Africa's mineral production and mineral resources.

In the discussions, Africa's annual production is given together with the annual world's production and the world's chief producer of the substance in question. Where available figures on African ore reserves are likewise included. There is a brief description of the occurrence but technical geological details are omitted. It is interesting to note that Africa leads the world in the mining of diamonds (99%), gold (40%), phosphates (36.6%) and radium ores, and is a large producer of copper (18%), chromium (31.6%), manganese (21.6%) and vanadium (47.5%). She has also large potential reserves of aluminum ore.

W. F. H.

NEW MINERAL NAMES

Ramsdellite

MICHAEL FLEISCHER AND WALLACE E. RICHMOND. The manganese oxide minerals: a preliminary report. *Econ. Geol.*, **38**, 269–286 (1943).

NAME: For L. S. Ramsdell, who first described the mineral (*Am. Mineral.*, **17**, 143–149 (1932)).

CHEMICAL PROPERTIES: Composition stated to be MnO_2. No analysis given. Inverts to pyrolusite when heated at 300° C.

PHYSICAL PROPERTIES: Orthorhombic. Color iron-gray to black. Streak black. Hardness 3, $G=4.7$. X-ray powder data are given.

OCCURRENCE: Occurs as thick tabular crystals and as massive material that has a platy appearance, owing to two cleavages at right angles. Commonly mixed with pyrolusite (transformation product?). Three localities are listed: Lake Valley, Sierra Co., N. Mex.; East River, Pictou Co., Nova Scotia; Kodjas Karil mine, Moustapha Pasha, Roumelia, Turkey.

MICHAEL FLEISCHER

NEW DATA

Coronadite, Cryptomelane, Hollandite, Lithiophorite, Ranciéite

FLEISCHER AND RICHMOND, *op. cit.*

X-ray powder data and a list of occurrences are given for all these minerals, with a brief summary of their physical properties. Lithiophorite and ranciéite, previously considered to be varieties of psilomelane, are independent species. No analyses are given, but the following formulas are tentatively suggested:

cryptomelane, KR_8O_{16}(?)
coronadite, PbR_8O_{16}(?) $R=Mn^4$ chiefly, also Mn^2, Co, Zn, Fe^3.
hollandite, BaR_8O_{16}(?)
lithiophorite, $Li_2(Mn^2, Co, Ni)_2Al_8\overset{4}{Mn}_{10}O_{35}\cdot 14H_2O$(?)
ranciéite, $(Ca, Mn^2)\overset{4}{Mn}_4O_9\cdot 3H_2O$(?)

DISCUSSION: In the *American Mineralogist*, **28**, 174 (1943), J. W. Gruner refers to material from Postmasburg, South Africa, as "corresponding to a new manganese mineral called oakite by W. E. Richmond. Oakite is found at White Oak Mt., Tenn."

The name oakite was a tentative designation for material later found to correspond to the old mineral lithiophorite. It is to be regretted that the name oakite accidentally found its way into print. The name oakite should be stricken from the literature.

M. F.

PROCEEDINGS OF SOCIETIES

NEW YORK MINERALOGICAL CLUB, INC.

Meeting of March 17, 1943.

Dr. A. C. Hawkins discussed "Mineral Collecting in the Southeastern United States," giving accounts of his collecting at various localities with emphasis on those in Georgia, North Carolina, and Virginia. Specimens from Dr. Hawkins' collection were exhibited.

Dr. Pough, on behalf of the Education Committee, announced that his classes in mineral identification had been successfully concluded and called attention to several recent publications of interest to mineralogists.

At the end of the meeting Mr. Edwin Skidmore of the New Jersey Mineralogical Club exhibited an improved ultra-violet lamp and many fluorescent specimens.

Meeting of April 21, 1943.

Mr. Archibald N. Goddard of Detroit entertained the members with many stories of his collecting experiences. Specimens exhibited included crystallized silver and copper, copper in calcite, and a splendid specimen of Chilean proustite which Mr. Goddard presented to the American Museum of Natural History.

The following officers were elected for the subsequent year:

PRESIDENT: Mr. James A. Taylor
1st VICE-PRESIDENT: Mr. F. H. Pough
2nd VICE-PRESIDENT: Dr. Robert B. Sosman
SECRETARY: Miss Elizabeth Armstrong
TREASURER: Dr. Cecil H. Kindle
DIRECTORS: Mr. John N. Trainer, Mr. Gilman S. Stanton.

Mr. Trainer announced the death on April fourth of Mr. John Vlismas.

Meeting of May 19, 1943.

Dr. Robert B. Sosman of the U. S. Steel Company Research Laboratories addressed the club on "Some Minerals of Professional Interest to the Steel Maker." He described the process of steel-making from the mining of the ore to the manufacture of the finished products and told what natural or artificial minerals are encountered at each step. Specimens of ores were exhibited including maghemite, a magnetic oxide of iron which closely resembles hematite in appearance. Dr. Sosman demonstrated the distinction between the two minerals by sprinkling the powder of each on a paper held over a magnet. Among the minerals produced in the blast furnace are anorthite, gehlenite, larnite, forsterite, and monticellite.

A tribute to the late Mr. Vlismas was read before the club by Mr. Sampter. Mr. Vlismas was a skilled "craftsman in stone" and created many unusual and beautiful things in his shop where club members were always welcome.

The retiring officers presented their annual reports and the incoming officers were installed at the end of the meeting.

Meeting of October 20, 1943.

In accordance with the club's custom the first meeting of the year was devoted to accounts of collecting and exhibits of material by members of the club. Travelling by train, bus and foot, many had visited interesting localities. Mr. and Mrs. E. L. Sampter collected mica, beryl, rose quartz, and feldspar crystals from the Scribner mine in Maine;

Dr. A. C. Hawkins collected titanite and tremolite from Easton; and Mr. and Mrs. E. J. Marcin found two-inch siderite crystals at Roxbury, Connecticut, that are now on display at the National Museum. Mr. L. A. Morgan displayed a large, deep purple cluster of amethyst crystals from Paterson, N. J., and hematite selectively crystallized on the prism faces of quartz crystals.

Other members exhibited specimens that they had bought or traded or collected in previous years.

ELIZABETH ARMSTRONG, *Secretary*

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